Reponse Techniques for the Cleanup of Sinking Hazardous Materials

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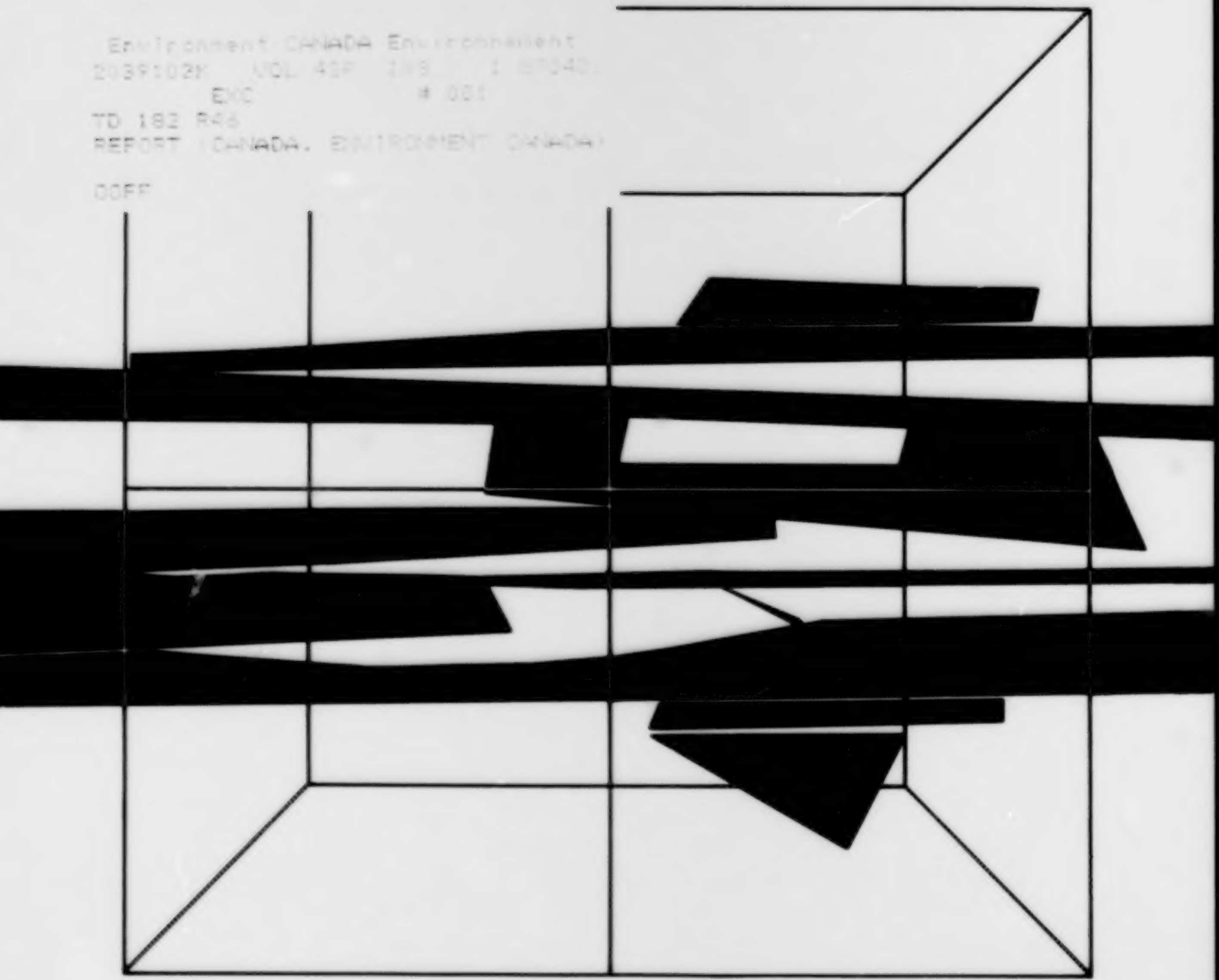

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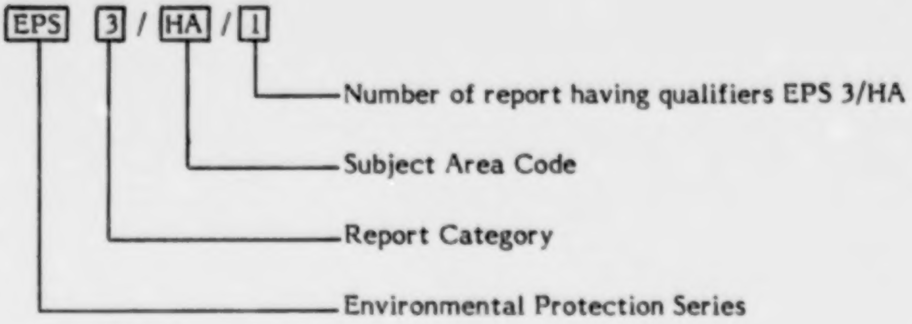
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RESPONSE TECHNIQUES FOR THE CLEANUP OF SINKING HAZARDOUS MATERIALS

by

Nancy Bonham

for the

Technology Development and Technical Services Branch
Environmental Protection
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ABSTRACT

Chemicals denser than water and having a low solubility are very difficult to deal with if accidentally spilled into water bodies. Chemicals in this category include aromatic organics, halogenated hydrocarbons, some organometallic compounds and the elements bromine and mercury.

Having a tendency to fall to or flow near the river bottom, the sinkers may permeate the sediments if they are in a liquid form. They can produce chronic toxic effects in aquatic flora and fauna. Difficulties are associated with their detection and cleanup.

The possible courses of action when dealing with this type of contamination are: leave it there, remove it for treatment, recover and dispose of it, or use in-situ physical/chemical treatment and/or isolation. These options and various techniques, their limitations and costs are examined in this report.

RÉSUMÉ

Les produits chimiques plus denses que l'eau et ayant une faible solubilité dans celle-ci causent de sérieux problèmes lorsque déversés accidentellement dans un cours d'eau. Ces produits comprennent les composés organiques aromatiques, les hydrocarbures halogénés, quelques composés organométalliques et les éléments brome et mercure. Ayant tendance à couler vers le fond des cours d'eau ils peuvent s'infiltrer dans les sédiments. Faune et flore aquatique risquent d'être affectées. En plus d'être difficilement détectables parce que physiquement séparés de la phase aqueuse, leur récupération est délicate.

Les solutions possibles à ce problème de contamination, autre que celle de ne rien faire, sont: l'enlèvement du contaminant et/ou de la masse de sédiments contaminés tout en minimisant la remise en solution, le traitement physique/chimique sur place et/ou l'encapsulation. Ces techniques sont discutées dans le rapport ainsi que leurs limites et leurs coûts.

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1 INTRODUCTION

"Sinkers" are chemicals that have a specific gravity greater than 1.0 and are relatively insoluble in water. Hazardous chemicals in this category are both solids and liquids and include organic and inorganic compounds such as: aromatic organics, halogenated hydrocarbons, some organometallic compounds and the elements bromine and mercury. As a group, these chemicals exhibit a wide range of physical and chemical properties and pose a variety of hazards.

"Sinkers" are among the most difficult chemicals to treat or recover when spilled in water. When a sinker enters water, it tends to fall or flow to or near the bottom and, if it is a liquid, it may permeate the sediments. The fact that the chemical has moved from the surface compounds the problems associated with detection and cleanup. Although the poor solubility of these chemicals normally leads to low levels of water contamination, they can subsequently enter the food chain through benthic organisms and produce chronic toxic effects in aquatic flora and fauna if not removed. The gradual dissolution of an untreated "sinker" could continue to contaminate the ecosystem for years.

The problems associated with the cleanup of contaminated river bottom sediments has been highlighted by the discovery of contaminants in the bottom sediments of the St. Clair River. Sediments containing toxic organic chemicals such as perchloroethylene, carbon tetrachloride, and hexachlorobenzene were identified near the Dow Chemical plant located on the St. Clair River near Sarnia, Ontario. During cleanup efforts, problems were encountered in removing the sediments without resuspending the contaminants and posing threats to the cleanup personnel.

1.1 Courses of Action

There are three possible courses of action that can be followed in dealing with spills of sinking hazardous materials:

1) take no action and allow the contaminant to remain in place;
2) remove sediments/contaminants to treat, recover and/or dispose; or
3) treat or isolate the contaminant in-situ using physical and/or chemical means.

Although 'no action' has been used in several documented cases, it is generally unacceptable because of the environmental and health threats posed. The mechanical removal of contaminants by pumping and/or dredging followed by treatment, recovery and/or disposal is the most popular choice and is recommended by many experts as the best amelioration technique (Ellis and Payne, 1983; Akers et al., 1981; Huibregtse et al., 1977). Isolation of contaminated sediments from the water column and in-situ treatment have received relatively little attention and are not considered to be established cleanup techniques.

1.1.1. Sediment/Contaminant Removal. Dredging of contaminated sediments poses numerous technical and economic problems including: the availability of suitable dredging equipment to remove contaminated sediments without resuspending contaminants and thereby increasing the threat to the aquatic species present; the ability to delineate the extent and depth of the contaminants present; the availability of techniques for the management of the dredge spoil; and the need to increase the efficiency and cost effectiveness of the dredging operations (Wetzel et al., 1984). Experience relating to these problems is minimal; there have been only a few documented incidents of dredging contaminated sediments in North America. Studies addressing these problems were conducted by the United States Environmental Protection Agency (EPA) and the U.S. Coast Guard.

1.1.2. In-situ Treatment. In-situ treatment is not recognized as an established technique because the chemical specific nature of most in-situ techniques make them appropriate for only a limited number of spill scenarios. Many mitigating agents are toxic themselves if used in excess; however, most amelioration agents require generous applications for timely results. Little information exists on the speed of action and relative effectiveness of individual in-situ treatment processes. The in-situ use of chemicals to mitigate hazardous spills can be justified only with proper controls and a thorough understanding of the possible harmful effects they may have on the environment. Some physical treatment techniques such as isolation by capping have only recently been recognized as an accepted disposal technique for contaminated sediment, and are subject to careful monitoring and research. Isolation through use of synthetic liners has been suggested but never field-tested.

Of the response techniques discussed, biodegradation and dispersion have the least potential. Opportunities for biodegradation are limited by the availability of an acclimated, chemical-specific culture and by the potential introduction or production of pathogens in the waterway. Dispersion should never be considered as the best response because of the threat to the environment and public health.

1.1.3. On-site Treatment. A number of mobile treatment units have been developed for spill response. Included are single and multi-component treatment units for the removal of suspended and dissolved organics. Through the use of physical and chemical techniques in series, the removal of most contaminants to accepted levels can be achieved within practical limits.

1.2 Reported Response Efforts

Spill response efforts for sinking chemicals have been limited, and documentation of these incidents is even more limited. A summary of documented spill response efforts is presented in Table 1 and summary of the efforts to cleanup contaminated sediments is found in Table 2.

1.3 Evaluation Matrices

Countermeasures appropriate for the various classes of soluble and insoluble sinkers are summarized in Tables 3 and 4. A matrix summarizing the extent of cleanup, the limitations, requirements, and costs of each amelioration technique is presented in Table 5.

TABLE 1 SPILL RESPONSE SUMMARIES (Bennet et al., 1982)

Hazardous Chemical	Containment	Recovery or Treatment
Oil and solvents containing 2% PCBs leached into nearby creek	- creek isolation using dams and a gravity bypass pipe	- excavation and removal of soils from pit area; leachate treated with carbon column using 2.8 m^3 of carbon preceded by disposable filter
Endrin, 18.6% in 3.8 L of pesticide into stream	- stream isolation using earthen dam at inlet to reservoir; sandbag dam at outlet, and stream diversion system	- first attempt: broadcasting 300 g of granular activated carbon on surface (failed); - second attempt: reservoir fluids pumped to carbon column (succeeded)
Phenol (80 000 kg), 5% into stream	- collection channel built to act as a reservoir to prevent runoff and leachate from entering stream	- flow from collection channel directed to carbon column using 28.3 m^3 carbon; clean underflow from carbon discharged to the stream
Transformer fluid (containing PCBs) runoff into creek	- booms	- powdered activated carbon, sedimentation and sand filtration
Dinitrobutylphenol into tributary	- spillway at outlet of lake dammed with sandbags	- treated with mixed-media filtration and activated carbon using EPA's mobile treatment system
Oil and 1% Pentachlorophenol (PCP; 3700 m^3) into stream	- none	- fluid pumped from recovery wells into vacuum trucks where oil-water separation occurred; water pumped to EPA mobile unit: sedimentation tank with oil skimming, filtration and carbon adsorption
Creosote into small stream	- none	- dredging of stream with Mudcat and hand-held devices; froth flotation and skimming using EPA mobile treatment unit
PCBs into bay	- none	- hand-held suction devices; settling tanks and flocculants to remove particulate; fluid treated with EPA's mobile unit using sedimentation, filtration, activated carbon
Pesticide (9.2 L) into stream (chlordane, heptachlor, petroleum derivatives)	- streamflow stopped downstream with earthen dam	- streamflow treated with EPA mobile unit
PCBs into bay	- none	- PCBs on ground absorbed with sawdust; sediments in bay covered with hog fuel (wood wastes) which was in turn covered with rock

TABLE 2 SUMMARY OF INCIDENTS OF SEDIMENT CONTAMINATION (Wetzel et al., 1984)

Description	Cleanup Technologies*	Comments
DUWAMISH WATERWAY (Seattle, WA) PCB-spill into tidal shipping channel tributary to Puget Sound	Pneuma dredge Air curtain Underwater hand-held dredge Settling tanks Settling impoundments Special landfill disposal On-site land disposal Sand filters Carbon adsorption	- cleanup conducted in two stages: initial emergency response and planned final cleanup; initial efforts did not achieve complete cleanup because of spread of contaminants by tidal action; cleanup employed EPA transportable physical/chemical treatment system (sand filters and activated carbon) and the Italian-made Pneuma dredge (a low-turbidity pneumatic dredge) (first application in U.S.)
GULF OUTLET OF MISSISSIPI RIVER (Shell Beach, LA) PCB-spill into tidal shipping channel tributary to Gulf of Mexico	Airlift dredge Settling barges Special landfill disposal Coagulation/flocculation Carbon adsorption	- airlift dredge was fabricated from locally available materials; divers were used to clear debris from the spill area; a Chromascope was used to locate bags of PCBs
HIRO HARBOUR (Kure-Shi, Japan) accumulation of nitrogen and ammonia in sediments of a coastal shipping port; attributed to long-term discharge of pulp waste	Cleanup dredge Settling barges Solidification Sanitary landfill disposal Coagulation/flocculation Carbon adsorption	- pilot-scale demonstration for future land reclamation project in the harbour; early demonstration of the Cleanup dredge (a low-turbidity hydraulic dredge)
JAMES RIVER (Hopewell, VA) accumulation of Kepone in sediments of a tidal shipping channel and commercial fishery tributary to Chesapeake Bay; attributed to long-term wastewater discharge	Cutterhead dredge Dustpan dredge Water column disposal Oozer dredge Settling impoundments Solidification On-site land disposal Carbon adsorption Photochemical degradation Ozonation Radiation Sorbents Capping	- feasibility studies followed by a comparative demonstration of the cutterhead and dustpan dredges (both hydraulic dredges) by U.S. Army Corps of Engineers; full-scale cleanup is unlikely; results of demonstration and monitoring of resulting turbidity provide information for evaluating needed maintenance dredging projects in the James River and other water bodies
MILL RIVER (Fairfield, CT) accumulation of lead in sediment of a small in-stream impoundment tributary to Long Island Sound; attributed to long-term industrial wastewater discharge	Portable hydraulic dredge Silt curtains Settling impoundments Filter press Solidification Special landfill disposal Sanitary landfill disposal Coagulation/flocculation Water column disposal Capping Fixation	- coagulating polymer used to promote settling of fine dredged solids; sediment disposed at both hazardous waste and sanitary landfill, depending on lead concentration; belt filter presses used to dewater sediments; mechanical problems caused by presence of debris (bricks, spikes) in sediment
NORTH FORK HOLSTON RIVER (Saltville, VA) accumulation of mercury in sediments of a small, fast-flowing rural river in industrial area; tributary to Tennessee River; attributed to long-term leakage from nearby industry	Stream diversion Cofferdams Dragline dredging Loader dredging Screening solids On-site land disposal Capping	- river flow was diverted using sandbag cofferdams; cofferdams were twice washed out by high river flows; fine (1/4-inch) screens clogged readily, 1/2-inch screens used successfully; screened material was 1/3 of total volume and contained 99% of recovered mercury; exposed river bottom was capped with hydraulically applied concrete
SOUTH BRANCH OF THE SHIAWASSEE RIVER (Howell, MI) accumulation of PCBs in sediments of a small, shallow rural river; tributary to Lake Huron; attributed to long-term discharge of industrial cooling water	Dragline dredging Backhoe dredging Above-water hand-held dredge Amphibious dredge In-stream turbidity control Settling tanks Solids separation by settling Special landfill disposal Sanitary landfill disposal Sand filtration Carbon adsorption Stream diversion Cofferdams Scraper dredging Filter press Solidification	- majority of sediment removed by vacuuming system operated by workers wading in the shallow river; removed sediments were separated into coarse and fine sizes by settling and filtering; sediment disposed at both hazardous waste and sanitary landfills, depending on PCB concentrations; in-stream dams were used to contain resuspended contaminated sediment

TABLE 2 SUMMARY OF INCIDENTS OF SEDIMENTS CONTAMINATION (cont'd)

Description	Cleanup Technologies*	Comments
SOUTH RIVER AND SOUTH FORK SHENANDOAH RIVER (Waynesboro, VA) accumulation of mercury in sediments of small and medium size rural rivers in Shenandoah Valley; tributary to Potomac River; attributed to long-term leaching of buried industrial waste	No action Stream diversion Cofferdams Amphibious dredge Special landfill disposal	- feasibility study resulting in 'no action' as the most favourable alternative; damage to river channel, costs, and projections of contaminant reduction by natural processes were major factors in the evaluation; responsible industry will monitor sediment, water, and fish for up to 100 years
STAMFORD AND NEW HAVEN HARBOURS (Stamford and New Haven, CT) accumulation of heavy metals in sediments of a commercial tidal shipping port tributary to Long Island Sound; sources of contaminants are not established	Clamshell dredging Capping	- contaminated sediments from Stamford Harbour were disposed in Long Island Sound and capped with clean sediments from New Haven Harbour; some erosion of the cap was observed, attributed to currents resulting from a major storm; evaluation of the effectiveness of the cap is in progress
UPPER HUDSON RIVER (Fort Edward, NY) accumulation of PCBs in sediments of a medium size rural river, part of NY State Barge Canal System; attributed to long-term industrial wastewater discharge	No action Clamshell dredging Backhoe dredging Loader dredging Cutterhead dredging Settling impoundments Special landfill disposal On-site land disposal Coagulation/flocculation Sorbents Capping Chemical treatment Biological treatment Stabilization/containment	- feasibility study for cleanup of submerged and floodplain contaminated sediments; capping and stabilization of floodplain sediments was recommended; additional mapping of contamination and no immediate cleanup action were recommended for the submerged sediments
WAUKEGAN HARBOUR (Waukegan, IL) accumulation of PCBs in sediments of a recreational boating harbour on west shore of Lake Michigan; attributed to long-term industrial wastewater discharge	No action Stream diversion Cofferdams Slurry wall Clamshell dredging Dragline dredging Backhoe dredging Scraper dredging Loader dredging Cutterhead dredging Dustpan dredging Hopper dredging Portable dredges Airlift dredging Pneuma dredging Oozer dredging Silt curtains Settling impoundments Settling barges Filter press On-site land disposal Coagulation/flocculation Sand filters Carbon adsorption Capping Fixation Chemical treatment Biological treatment	- exhaustive feasibility study resulting in recommendation of slurry wall containment, dredging and capping, fixation, and disposal in a chemical waste landfill; various alternatives and subalternatives were developed from over 70-unit processes
PORPOISE HARBOUR (Prince Rupert, B.C.) PCB-spill into storm drain leading into harbour	Removal In-situ containment	- PCBs on ground absorbed with sawdust; sediments in bay covered with hog fuel (wood wastes) which in turn was covered with rock.

* Underscored technologies were implemented; remaining technologies were considered as alternatives.

TABLE 3 SOLUBLE SINKERS IN WATER (Unterberg et al., 1984)

	Applicable Countermeasures																						
	Containment				Displacement			Treatment															
Chemical Class	Dikes, Berms, Dams	Trenches	Curtain Barriers	Stream Diversion	Dredging -Mechanical (1)	Pumping	Dispersion/Dilution (2)	Activated Carbon	Natural Inorganic (3)	Sorbents	Synthetic Sorbents	Gravity Separation	Membrane Separation	Coagulation/Flocculation	Extraction	Chelation/Sequestration	Ion Exchange - Anionic	Ion Exchange - Cationic	Neutralize w/acid (5)	Neutralize w/base (6)	Oxidation	Precipitation (6)	Biological Treatment (7)
Acids, organic	x	x	x	x	x	x	x	x				x	x		x					x			x
Acids, inorganic	x	x	x	x	x	x	x					x	x		x		x			x			
Alcohols and glycols	x	x	x	x	x	x	x	x				x	x		x						x		
Aldehydes	x	x	x	x	x	x	x	x				x	x		x						x		x
Aliphatics, halogenated	x	x	x	x	x	x	x	x				x	x		x						x		
Amides, onilides and imides	x	x	x	x	x	x	x					x	x		x								
Amines, alkyl	x	x	x	x	x	x	x					x	x		x								
Amines, aryl	x	x	x	x	x	x	x	x				x	x		x								x
Aromatics	x	x	x	x	x	x	x	x				x	x		x								x
Aromatics, halogenated	x	x	x	x	x	x	x	x				x	x		x								x
Azo compounds	x	x	x	x	x	x	x					x	x		x								
Caustics	x	x	x	x	x	x	x	x				x	x		x				x		x		
Chromates	x	x	x	x	x	x	x	x				x	x		x		x	x				x	
Cyanates	x	x	x	x	x	x	x					x	x		x			x					
Cyanides and nitriles	x	x	x	x	x	x	x	x				x	x		x		x	x			x		x
Epoxides	x	x	x	x	x	x	x					x	x		x								
Esters	x	x	x	x	x	x	x					x	x		x		x						
Ethers	x	x	x	x	x	x	x					x	x		x								
Halides, alkyl	x	x	x	x	x	x	x					x	x		x	(4)							
Halides, inorganic	x	x	x	x	x	x	x	x				x	x		x	x	x	x				x	
Heavy metals	x	x	x	x	x	x	x	x	x			x	x	x	x	x	x	x		x	x	x	
Hydrazines and hydrolazides	x	x	x	x	x	x	x					x	x		x				x				
Ketones	x	x	x	x	x	x	x					x	x		x								x
Nitromycin	x	x	x	x	x	x	x					x	x		x								
Nitrates and nitriles	x	x	x	x	x	x	x	x				x	x		x			x			x	x	
Nitro compounds	x	x	x	x	x	x	x					x	x		x								
Nitroso compounds	x	x	x	x	x	x	x					x	x		x								
Organic Ammonium compounds	x	x	x	x	x	x	x					x	x		x		x	x	x				
Organo metallics	x	x	x	x	x	x	x	x				x	x		x		x	x		x		x	
Organo phosphates	x	x	x	x	x	x	x	x				x	x		x					x			
Oxides	x	x	x	x	x	x	x	x				x	x		x							x	
Peroxides	x	x	x	x	x	x	x					x	x		x								
Phenols and cresols	x	x	x	x	x	x	x	x			x	x	x	x	x		x			x	x		x
Phosphates and phosphonates	x	x	x	x	x	x	x	x				x	x		x				x	x			
Phosphorus and compounds	x	x	x	x	x	x	x	x				x	x		x			x		x			
Streptozotocin	x	x	x	x	x	x	x	x				x	x		x								
Sulphates	x	x	x	x	x	x	x	x				x	x		x			x		x		x	
Sulphides and mercaptans	x	x	x	x	x	x	x	x				x	x		x		x				x		
Sulphites	x	x	x	x	x	x	x	x				x	x		x		x	x			x		
Sulphones, sulphoxides and sulphonates	x	x	x	x	x	x	x	x				x	x		x		x						
Ureas	x	x	x	x	x	x	x					x	x		x								

(1) Applicable to immobilized masses of particulate only.
(2) Reduce contaminant levels below toxic level through flow augmentation, mechanical mixing, or chemical dispersants. Applicable to small spills in remote areas only!
(3) Metal oxides and glauconitic greensands.
(4) Excluding ammonium halides.
(5) Treatment with sodium bicarbonate or lime recommended.
(6) Treat with stoichiometric amounts of sulphide except chromates; treat chromates with bisulphite.
(7) Potentially biodegradable.

TABLE 4 INSOLUBLE SINKERS IN WATER (Unterberg et al., 1984)

	Applicable Countermeasures																			
	Containment					Displacement			Treatment											
Chemical Class	Dams, Berms and Dikes	Trenches	Curtain Barriers (1)	Stream Diversion	Synthetic Membrane Covers	Dredging (2)	Pumping	Dispersion/Dilution (3)	Activated Carbon	Synthetic Sorbents	Granular Media Filtration	Gravity Separation	Coagulation/Flocculation	Ion Exchange -Anionic	Ion Exchange -Cationic	Neutralize w/acid (4)	Neutralize w/base	Oxidation	Precipitation	Biological Treatment (7)
Acids, organic	x	x	x	x	x	x	x	x	x		x	x					x			
Aliphatics, halogenated	x	x	x	x	x	x	x	x	x	x	x	x						x		
Amides, onilides and imides	x	x	x	x	x	x	x	x			x	x								
Amines, alkyl	x	x	x	x	x	x	x	x	x		x	x						x		
Amines, aryl	x	x	x	x	x	x	x	x	x		x	x						x		
Aromatics	x	x	x	x	x	x	x	x	x		x	x						x		
Aromatics, halogenated	x	x	x	x	x	x	x	x	x	x	x	x					x	x		
Asbestos	x	x	x	x	x	x	x	x			x	x								
Azo compounds	x	x	x	x	x	x	x	x			x	x								
Caustics	x	x	x	x	x	x	x	x	x		x	x				x				
Chromates	x	x	x	x	x	x	x	x	x		x	x		x					x	
Cyanates	x	x	x	x	x	x	x	x	x		x	x		x	x			(5)		
Cyanides and nitriles	x	x	x	x	x	x	x	x	x		x	x		x	x		x	x		
Epoxides	x	x	x	x	x	x	x	x	x		x	x						x		
Esters	x	x	x	x	x	x	x	x	x		x	x								
Ethers	x	x	x	x	x	x	x	x	x		x	x								
Halides, alkyl	x	x	x	x	x	x	x	x	x		x	x								
Halides, inorganic	x	x	x	x	x	x	x	x	x		x	x		x	x		x		x	
Heavy metals	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x				x	
Ketones	x	x	x	x	x	x	x	x	x		x	x								
Nitro compounds	x	x	x	x	x	x	x	x	x	x	x	x						x		
Nitroso compounds	x	x	x	x	x	x	x	x	x		x	x								
Olefins	x	x	x	x	x	x	x	x	x		x	x								
Organo metallics	x	x	x	x	x	x	x	x	x		x	x		x	x				x	
Organo phosphates	x	x	x	x	x	x	x	x	x		x	x								
Oxides	x	x	x			x	x	x	x		x	x			x			x		
Peroxides	x	x	x			x	x	x			x	x					x	(5)		
Phenols and cresols	x	x	x			x	x	x	x	x	x	x	x					x		x
Phosphorus and compounds	x	x	x			x	x	x			x	x		x	x					
Phosphates and phosphonates	x	x	x			x	x	x			x	x								
Strychnine and salts	x	x	x			x	x	x	x		x	x								
Sulphates	x	x	x			x	x	x			x	x			x					
Sulphides and mercaptans	x	x	x			x	x	x	x		x	x		x	x			x		
Sulphites	x	x	x			x	x	x			x	x								
Sulphones, sulphoxides and sulphonates	x	x	x			x	x	x	x		x	x		x						
Ureas	x	x	x			x	x	x			x	x								

(1) Use during dredging operations.
(2) Mechanical dredging applicable to particulates only.
(3) Reduce containment levels below toxic level through flow augmentation and mechanical mixing. Applicable to small spills in remote areas only!
(4) Treat with dilute and/or removable acids.
(5) Treat with sodium or calcium hypochlorite.
(6) Treat with hydrogen peroxide or ozone.
(7) Potentially biodegradable.

TABLE 5 SUMMARY OF COUNTERMEASURE LIMITATIONS, REQUIREMENTS AND COSTS (adapted from Unterberg et al., 1984)

					Limitations							Requirements							
Countermeasure	Mode	Potential Extent of Cleanup	Form of HS	Dependent Time (days)	Wind	Precipitation	Temperature	Water Velocity	Water Surface Cond.	Special Access	Unusable in Populated Area	Special Equipment	Power	Monitoring	Off-site Disposal/ Recycling	Special Safety Precautions	Manpower	Cost	Comments
Curtain barrier	IS	NA	N D	>1	x			x	x			x					6T	$\$60$ to $\$90/\text{m}$	Max. current 1 knot; max. depth 7.6 m; max. waves 2.3 m.
Dams, berms, dykes	IS	NA	N D	V	x			x	x	x		x						$\$3/\text{m}^3$	Confined to quiescent and nearshore areas.
Trenches	IS	NA	N D	V	x			x	x	x		x						$\$3.80$ to $\$11.5/\text{m}^3$	Confined to quiescent and nearshore areas.
Stream Diversion	IS	NA	N D	V		x		x		x		x	x						Stream must have relatively low flow rates.
Burial	IS	NA	D	>1	x			x	x	x		x		x				$\$1.80/\text{m}^3$ +	Inappropriate for liquid pools. Re-exposure may occur.
Synthetic Membrane Cover	IS	NA	N D	V	x			x	x	x		x						$\$12$ to $\$24/\text{m}^2$	Material must be chemically compatible with hazardous substance. Navigable water only.
Dispersion/ Dilution	IS	G	N	V				x			x								Bad weather and rough water enhance dispersion.
Dredging	IS	G	N	>1	x			x	x	x		x			x			$\$1.95/\text{m}^3$	Must know perimeter of spill.
Pumping	IS	G	N D	V	x			x	x	x		x	x		x				9.8 m height limit unless booster pumps are used.
Sorbents (Natural & Synthetic)	IS	G	N	<1	x			x	x	x					x				Sorbent must sink and be hydrophobic.
Sorbent Column	OS	MP	D	>1						x		x	x	x	x				Spent sorbent must be regenerated and/or disposed of.
Gelling Agent	IS	G	D N	<1	x			x	x	x					x			$\$14.3/\text{kg}$	
Gravity Separation	OS	G	N	<1						x		x	x	x	x		2T		Follows precipitation or flocculation and precedes polishing.
Granular Media	OS	G	N	>1								x	x	x	x				Follows flocculation and precedes polishing.
Membrane Separation	OS	P	D	>1						x		x	x	x	x		2T		Should be preceded by filtration.
Neutralization	IS	MP	N D	<1	x		x	x	x					x		x			Neutralizer itself may be hazardous to the environment.
Neutralization	OS	MP	N D	<1						x		x	x	x		x			
Precipitation	IS	GP	D	<1	x		x	x	x					x	x				Precipitating chemicals may be hazardous. Toxic precipitates should be removed by dredging and disposed of.
Precipitation	OS	GP	D	<1						x		x	x	x	x	x			Precipitants may be hazardous.
Coagulation/ Flocculation	OS	M	D	>1/2						x		x	x	x	x				Usually followed by filtration or gravity separation.
Solvent Extraction	OS	M	D	<1						x		x	x	x	x				Proper choice of solvent very important.
Oxidation	IS	MP	D	<1	x			x	x							x			Oxidants and/or reaction products may cause environmental damage. May require pH adjustment.
Oxidation	OS	MP	D	<1						x		x	x	x		x			
Biological Treatment	IS	MP	D	>1			x	x	x					x					May require special cultures. May introduce pathogens.
Biological Treatment	OS	MP	D	>1						x		x	x	x	x				May require special cultures.

On-site	MP	Moderate Polish	N	Neat
In-situ	G	Gross	V	Varies
Moderate	D	Dissolved	T	Technician

2 DREDGING

Dredging techniques are the logical and perhaps only feasible means for the recovery of spilled hazardous materials resting on the bottom of a waterway. Dredging alone, however, can seldom be expected to accomplish total recovery of the spilled chemicals and should be considered in conjunction with other measures such as burial or *in-situ* chemical treatment. The latter techniques are particularly applicable around the periphery of a spill where contaminant levels are too low to justify continued dredging. In addition to the recovery of the contaminant, dredges can be used to build barriers such as trenches or dykes to prevent dispersion. Dredging should always be considered as a follow-up technique after burial or use of sorbents.

Maximizing the rate of sediment removal has been the major focus in the development of dredging equipment and practices. More recently, the environmental effects of dredging have also received attention. Traditionally, the type of equipment and methods used in a given job have been based on:

- the type and amount of sediment to be dredged;
- the physical and hydrologic characteristics of the dredging site;
- the water depths in the area to be dredged;
- dredged material disposal considerations; and
- the availability of dredging equipment.

Modifications to existing equipment and operating methods must and are being made to accommodate the removal of contaminated sediments. Both in the United States and abroad, new specialized dredging equipment is being developed with the objective of reducing environmental effects. Additional factors that must be considered when dredging contaminated sediments include:

- the need for precise determination and boundary marking of the area to be dredged;
- the need for precise lateral and vertical control of the dredging head;
- the requirement for special precautions tailored to specific chemicals;
- the need to reduce and eliminate the resuspension of contaminated sediments (particularly clay-sized and organic particles, which are associated with the majority of contaminants);
- the need to predict the likely damage to aquatic and benthic organisms; and
- the requirement for temporary storage, transport, and treatment prior to disposal of the dredged material.

Actual "hands-on" experience relating to these problems is minimal as there have only been a few documented contaminated sediment dredging operations (Wetzel et al., 1984).

Before 1970, when little was known about the environmental effects of dredging and dredged material disposal, regulations on disposal were often excessive and counterproductive. In 1973, the United States Congress directed the U.S. Army Corps of Engineers to undertake a comprehensive research program to develop procedures for determining the environmental consequences of dredged material disposal and to develop new or improved methods for minimizing adverse effects. As a result, much work has been conducted in the United States over the past ten years on the effects of disposal. Conversely, little work has been undertaken on the effects of the dredging operation itself, as it was assumed that disposal would have the most significant impact. Only recently has the need been recognized to develop procedures and/or equipment that will minimize the adverse effects of the dredging operation. The U.S. Army Corps of Engineers, under the Improvement of Operational and Maintenance Techniques (IOMT) Research Program, collected data (national and international) on the resuspension of sediments and contaminants. Field studies were considered at various sites where unconventional equipment is being used. The overall objective was to develop guidelines for the dredging of highly contaminated sediments.

Dredge selection in a particular spill situation depends on numerous factors, including: the size of the spill; location (e.g., river, harbour, or lake); the depth to be dredged; the form of contaminant (liquid or solid); and environmental constraints. The particular chemical involved in the spill will seldom be a factor in choosing the best equipment for the job, except in cases where the contaminant is present as an intact mass. It has been observed that the specific gravity of the spilled material has a definite effect on recovery efficiency.

Management of the large volume of dredged material poses numerous problems. Dredged slurries, with solids contents generally in the order of 10 to 20% by weight, require extensive dewatering followed by the chemical treatment of a large volume of supernatant. Dewatering of the dredge spoil can usually be accomplished on-site by conventional solids concentration technology. Chemical treatment can be achieved in one of the many mobile treatment units available. Hansen and Sanders (1981) indicate that placement in an approved sanitary landfill is the sludge disposal method that has the widest applicability. For very toxic substances, the sludge should be securely packaged in barrels.

2.1 Dredge Types

Dredges are classified in various ways according to:

1) their basic means of moving material (i.e., mechanical or hydraulic);
2) the method of storage or deposition of dredged material (i.e., pipeline, sidecaster, hopper);
3) the device used for excavating sediments (i.e., cutterhead, dustpan); and
4) the type of pumping device used (i.e., centrifugal, pneumatic, or airlift).

Dredges generally do not come in standard models but are designed for a specific jobs. Classifications used in this report are: mechanical, hydraulic, pneumatic, and special purpose dredges.

2.1.1 Mechanical Dredges. Mechanical dredges such as the grab or clamshell, the dipper, and bucket ladder are designed for hard or soft material and normally are not self-propelled. They remove bottom sediment by direct application of mechanical force to the bottom surface, and they excavate the material at nearly in-situ densities, thereby limiting the amount of material to be handled. As no provision is made for material containment, most mechanical dredges deposit the material into scows or barges for transportation to the disposal site. They can be controlled and manoeuvered in small and confined areas and are useful in areas with obstructions and debris.

Mechanical dredges, however, are only capable of only modest production rates (<500 m^3/h) and require separate disposal vessels and equipment. These dredges cause a great deal of sediment resuspension and are ineffective against free or unabsorbed liquid contaminant.

Grab or clamshell. Grab or clamshell dredges are crane-operated devices used to excavate most types of material with the exception of solid rock (Figure 1). These dredges excavate a heaped bucket of material, some of which is washed away by drag forces during hoisting. The Japanese have designed an enclosed bucket that reduces the problem of fines and loose material escaping, but this modification has not been used in North America.

Clamshell buckets range in capacity from 0.75 to 9.0 m^3 and are capable of operating at 20 to 30 cycles per hour, depending on the water depth and the substrate characteristics. The working depth is theoretically limited only by the cable length and most are capable of working in depths to 30 m or more. These dredges are frequently

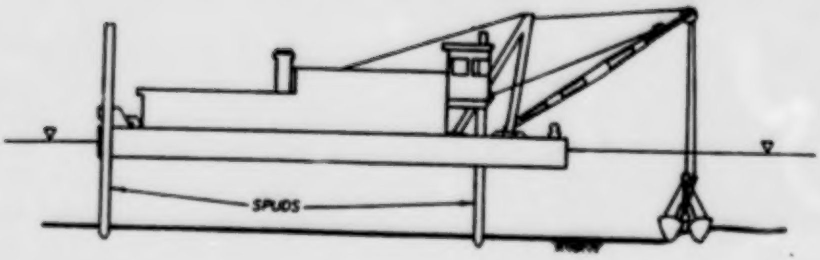


FIGURE 1 CLAMSHELL DREDGE (Hand et al., 1978)

used in confined areas where the control of the position and depth is essential. There are 52 clamshell/grab dredges in Canada.

Dipper. Dipper dredges are frequently used in subaqueous excavation of soft broken rock and dense sedimentary deposits (Figure 2). They may cause significant sediment disturbance during digging and loss of fines from the bucket during the hoisting process. Bucket capacity ranges from 0.75 to 12 m^3 and the working depth is up to 15 m. The production rates vary from 30 to 60 cycles per hour.

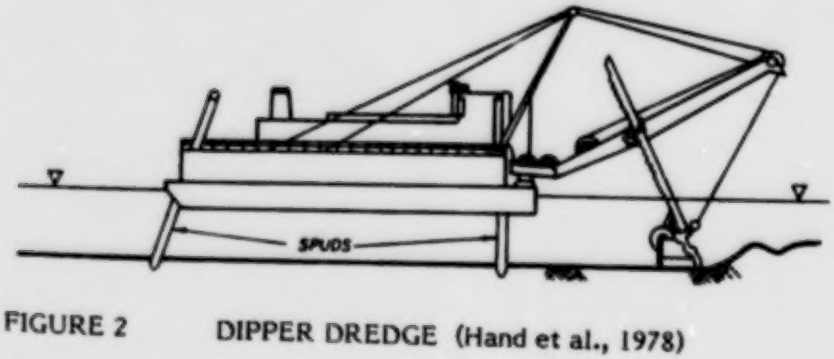


FIGURE 2 DIPPER DREDGE (Hand et al., 1978)

Bucket ladder. The bucket ladder dredge has an inclined ladder that supports a continuous chain of buckets that move around two tumbler pivots (Figure 3). As the buckets revolve around the lower tumbler, material is scooped, transported up the ladder, and dumped into a trough. As with the other mechanical dredges, considerable loss of fines occurs.

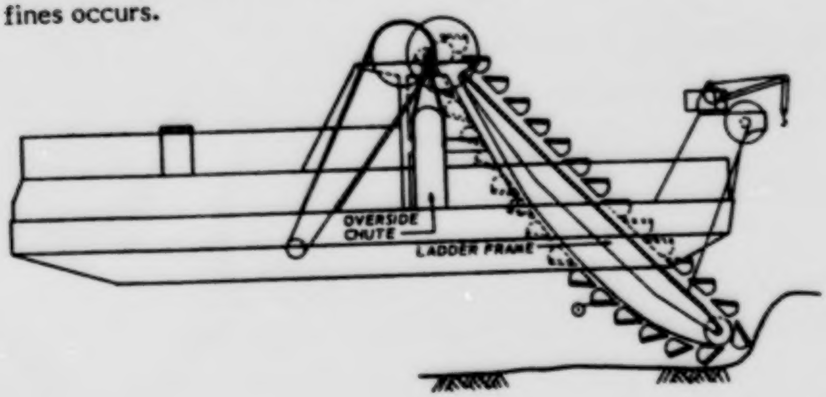


FIGURE 3 BUCKET LADDER DREDGE (Hand et al., 1978)

2.1.2 Hydraulic Dredges. Hydraulic dredges such as the suction, dustpan, cutterhead and hopper, remove and transport sediment in liquid slurry form. Depending on the size, they are capable of the highest production rate of any dredge (up to 11 500 m^3/h). They are usually barge-mounted and carry-diesel or electric-powered centrifugal pumps with discharge pipes ranging from 15 to 122 cm in diameter. The slurries, usually containing 10 to 20% solids by weight, are often transported several thousand metres through pontoon-supported pipelines to the disposal site. Using pipelines to directly transport the material to the disposal site minimizes handling of and exposure to the contaminated dredged material. Other material handling methods include sidecasting, loading into barges or scows, and direct loading of onboard hoppers.

These types of dredges have a number of limitations:

- barge-mounted dredges cannot be employed in rough waters;
- the large volume of water requires major dewatering and consolidation operations for disposal;
- cutterhead and suction lines are hindered and possibly damaged by underwater debris, large rocks and other obstacles;

- the deep draft of hopper dredges precludes their use in shallow waters;
- hopper dredges cannot operate continuously;
- full hopper capacity cannot be used when excavating contaminated sediments due to potential overflow of contaminated water;
- hopper dredges operate with less precision than other dredge types; and
- open-water dumping cannot be used for contaminated sediments.

Suction dredge. The suction dredge relies on the suction generated by a centrifugal pump to dislodge, capture and transport the excavated slurry (Figure 4). It is most useful in pumping free-flowing materials such as sand or unconsolidated sediments. The dredge has no digging devices and is not useful against hard or cohesive bottom materials.

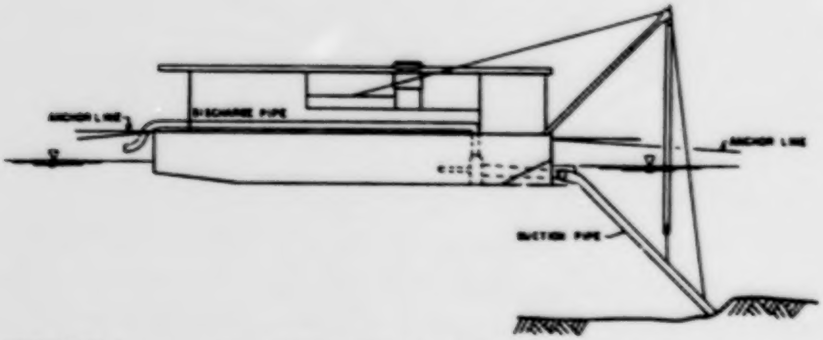


FIGURE 4 PLAIN SUCTION DREDGE (Hand et al., 1978)

Plain suction dredges are commonly used for sand mining, beach restoration, river channel maintenance and scow unloading. The production rate is a function of the pipe size, the pump horsepower, and the type of material being dredged.

Dustpan dredge. The dustpan dredge is a hydraulic suction dredge that uses a widely-flared dredging head along which high-pressure water jets are mounted (Figure 5). The jets loosen the sediments which are then captured in the dustpan head as the dredge is winched forward. The high pressure jets allow cohesive sediments to be dredged but they also produce considerable resuspension of the material into the water column.

Pipeline diameters range from 0.6 to 1.2 m. A dustpan dredge with a 0.8-m diameter pipeline has a production rate of 2676 m^3/h and can operate in depths to 18 m.

Cutterhead. The cutterhead is unique in that it has a powerful rotating mechanical digging apparatus mounted at the intake of the suction pipe (Figure 6). The

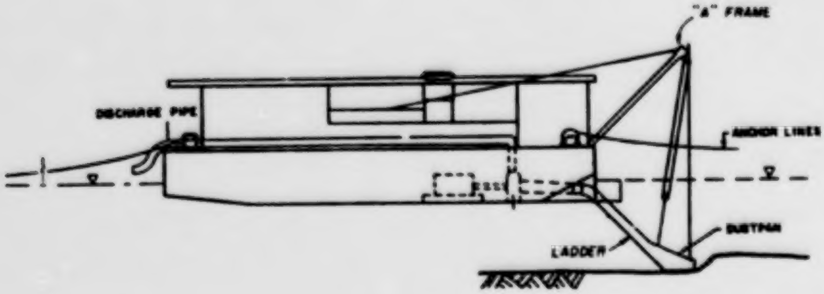


FIGURE 5 DUSTPAN DREDGE (Hand et al., 1978)

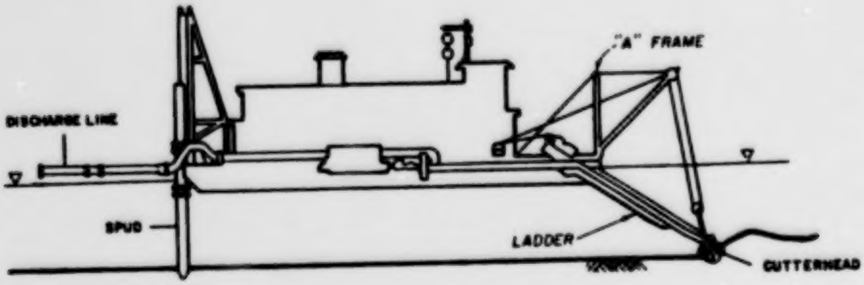


FIGURE 6 CUTTERHEAD DREDGE (Hand et al., 1978)

cutterhead breaks up hard and cohesive materials to create a slurry that can be transported by pipeline. When the cutterhead is shut off, it behaves as a plain suction dredge. The pipeline diameters range from 15 to 76 cm with production rates varying from 19 to 1900 m^3/h. The dredging depth varies from 3.6 to 15 m, respectively.

Hopper. Hopper dredges differ from other suction dredges in that they are mounted on self-propelled, sea-going vessels instead of barges (Figure 7). The suction pipes are hinged on each side of the ship with the intake extending downward toward the stern of the vessel. The head is dragged along the bottom as the vessel moves forward at speeds up to 13 km/h. The material is lifted up the suction pipe and stored in the hold or hopper of the ship. Excess water containing a high level of suspended solids is allowed to flow over weirs in the hoppers and back into the waterbody. The excavation of

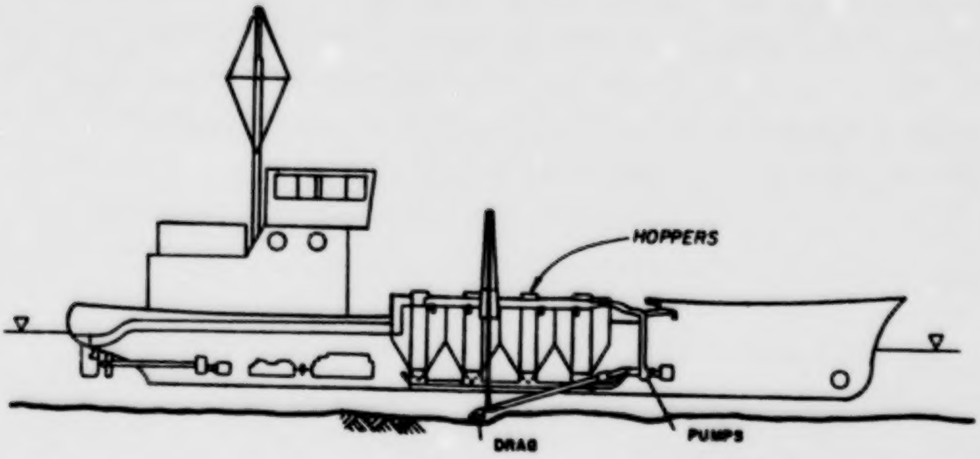


FIGURE 7 HOPPER DREDGE (Hand et al., 1978)

contaminated sediment would require the overflow of the hoppers to be eliminated. Unloading is normally accomplished by dumping the material back into the waterbody at a different location. For contaminated dredged material, pumping out of the hoppers to a safe disposal site would be necessary. Some hopper dredges are equipped with built-in pump-out capability while others require the use of auxiliary equipment.

Hopper dredges are most efficient in excavating loose, uncohesive materials. It is the only dredge capable of operating in rough open waters, in relatively high currents, in and around marine shipping traffic, and in adverse weather conditions.

Hopper dredge slurries have a solids content of 10 to 20%. The vessel drafts range from 3.6 to 9.5 m with production rates ranging from 380 to 1530 m^3/h. The minimum dredging depth varies from 3 to 8.5 m with the maximum dredging depths being 20 m.

2.1.3 **Pneumatic Dredges.** Pneumatic dredges are hydraulic pipeline systems that use a compressed air-operated pump (Figure 8). The "Pneuma," developed in Italy, consists of a pneumatic pump suspended on cables from a barge-mounted crane. The pump consists of three cylinders that are alternatively filled with sediment by hydrostatic pressure. When the cylinders are full, they are serially emptied by closing the inlet and applying compressed air to force the contents into a common header line. The primary advantage is that the sediment does not have to be in liquid slurry form. Materials handling problems and turbidity are minimized.

There is no theoretical depth limitation to the pneumatic pump and, because it is crane-mounted, it is useful in and around port structures. However, cables and pipelines can present temporary obstructions in navigable waterways and they have modest production rates (46 to 300 m^3/h). The system is not small, but it has the advantage of being broken down into components that are truck- or air-transportable.

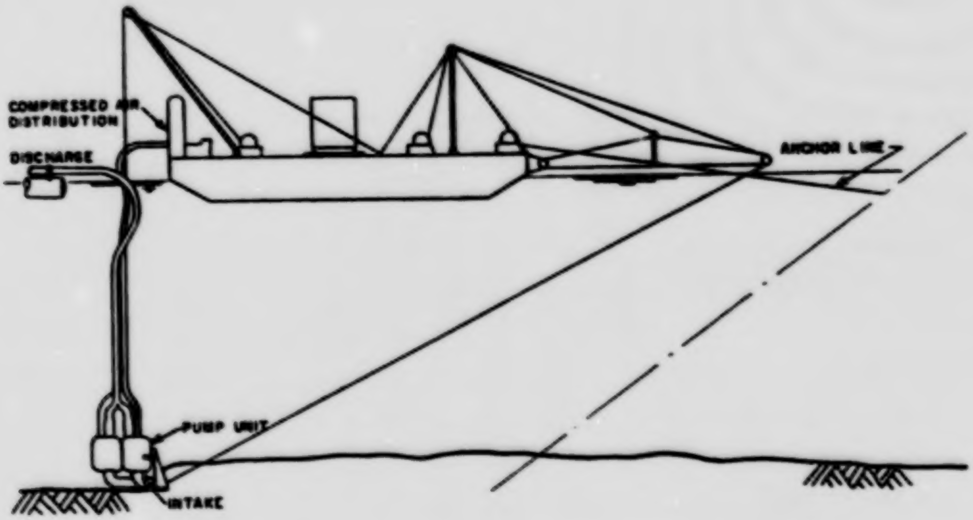


FIGURE 8 PNEUMA DREDGE (Hand et al., 1978)

2.1.4 Special Purpose Dredges.

Hand-held vacuum units. Hand-held suction devices manipulated by a diver, with a pump and storage tank on board either a barge, a boat or land-based truck are considered invaluable in the dredging of intact masses of solid or liquid contaminant. One month after a PCB spill in the Duwamish River, hardhat divers recovered 30% of the material by dredging the bottom mud up to 0.5 m deep (Hand et al., 1978). Principal advantages of hand-held suction devices include: 1) extreme mobility and universal availability; 2) manual positioning, which allows meticulous cleanup work; and 3) effectiveness in vacuuming identifiable masses of pure contaminant, particularly liquids and free-flowing solids. The major drawback is the risk of contaminant exposure for the hardhat diver. The U.S. government has conducted an extensive evaluation of diver safety at spills of hazardous materials.

Hand-held vacuums have low production rates (~ 10.6 m^3/h) but they can operate in depths up to 31 m with low turbidity. The solids concentration of the pumped slurry is generally 5 to 10% by weight.

Oozer dredge. The Oozer dredge, manufactured in Japan by Toyo Construction Co., Ltd., is a pneumatic dredge specially designed for dredging contaminated sediments (Figures 9 to 11). Its ability to achieve a high solids-to-water ratio in the slurry (up to 80% of that in-situ) with minimal resuspension, make it ideally suited for this purpose. It has been experimentally determined that to remove a given thickness of sediment to be dredged, it is necessary to remove an excess thickness of 20%. Dredging accuracy is improved by a mechanism that keeps the suction mouth parallel to the seabed (Figure 11).

The Oozer dredge has a capacity ranging from 350 to 500 m^3/h and can operate in depths up to 46 m.

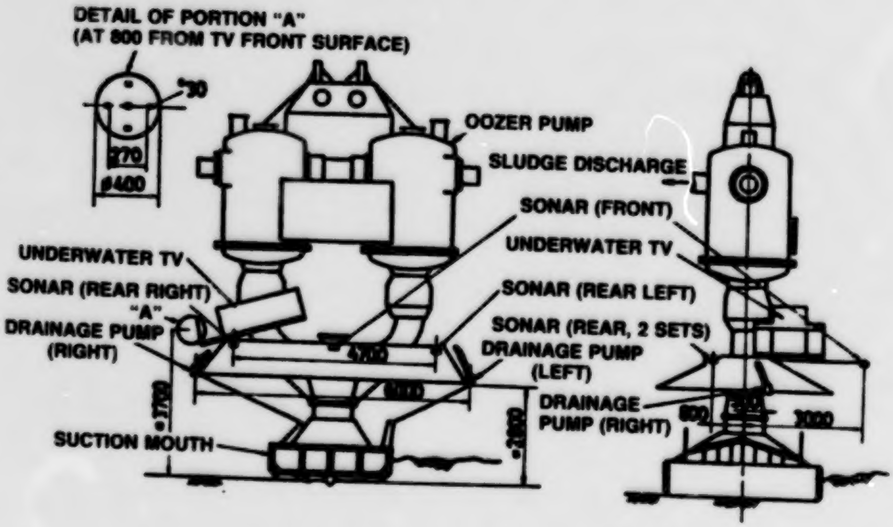


FIGURE 9 OOZER DREDGING MECHANISM
(lengths in mm) (Koba and Shiba, 1981)

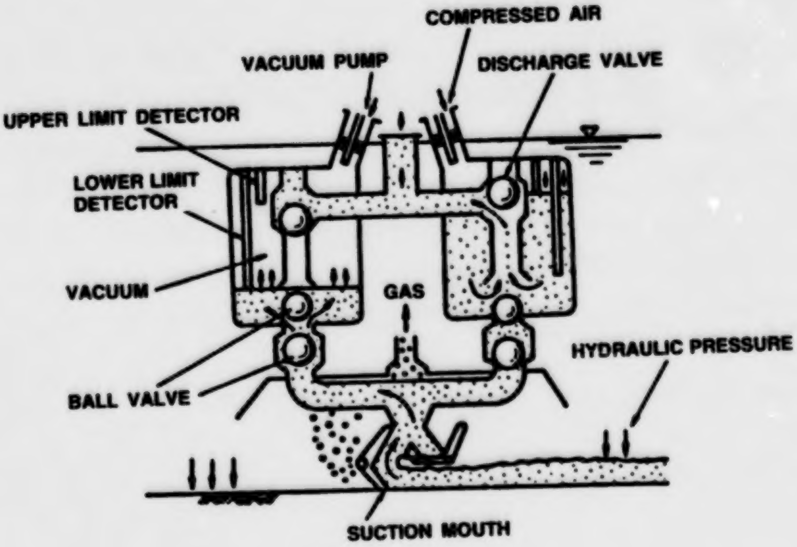
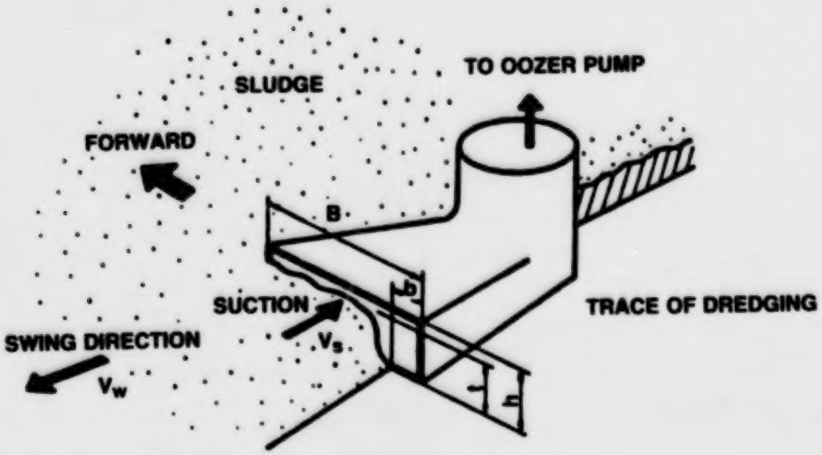


FIGURE 10 OOZER PUMP OPERATION (Koba and Shiba, 1981)



Symbols

B - suction mouth width

b - overlap width of suction mouth

V_w - swing speed

h - height of suction mouth

t - sucked soil thickness

V_s - suction velocity

FIGURE 11 CUTTERLESS SUCTION MOUTH MODEL (Koba and Shiba, 1981)

Refresher system. Produced by Penta Ocean Construction of Japan, the Refresher system is a conventional cutter-suction dredge that has been modified for the cleanup of toxic sediments. The system was developed to ensure the prevention of generation and dispersion of turbidity and the complete removal of the bottom sediments. Turbidity can be monitored by an underwater TV camera and can be measured by a turbidimeter.

The capacity of the Refresher system is 150 to 1000 m^3/h with a solids concentration of 30 to 40% by weight. The working depth ranges from 6 to 18 m.

Mudcat. The Mudcat is a portable hydraulic dredge that was designed and developed by the U.S. National Car Rental Agency (Figure 12). The machine is mounted on pontoons and features an auger-like cutting device that feeds the slurry to the suction intake of a centrifugal pump. The dredge is propelled along an anchored cable and the dredged material is discharged through a float-supported pipeline.

The mudcat has been used in several incidents of contaminated sediment cleanup and has been studied by the U.S. EPA (Nawrocki, 1976). Nawrocki (1976) concluded that the Mudcat was effective in removing particulate matter from pond bottoms. During that study, the Mudcat was shown to have a greater removal efficiency in a backward cut than in a forward cut. The explanation given was that during a backward cut the mudshield was fully extended over the auger and thus was more effective in decreasing turbidity. Nawrocki (1976) also found that the specific gravity of the spilled material influenced the recovery efficiency. As the specific gravity increased, the recovery efficiency increased and the contaminant resuspension decreased.

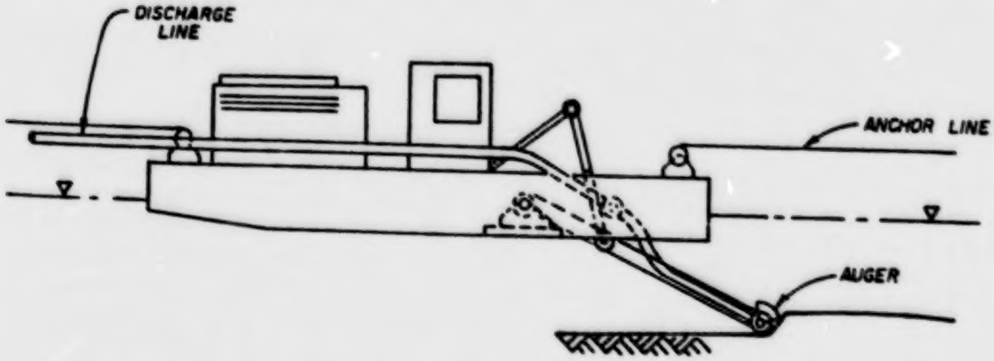


FIGURE 12 THE MUDCAT DREDGE (Hand et al., 1978)

The Mudcat's size and production capacity limit it to small jobs; production rates are up to 92 m^3/h in depths no greater than 6.1 m. The principal advantage of this unit is that its compact size makes it readily transportable by truck or air to operate in confined and isolated areas.

2.2 Dredge System Evaluation

The important operating characteristics, capabilities and limitations of the dredges previously discussed are summarized in Table 6. The wide range of values under some parameters reflects the large number of units of varying size. Table 6 is a valuable tool in making a quick assessment of the suitability of a particular dredge for a specific spill situation. This table should be used in conjunction with the dredge evaluation matrices presented in Tables 7 to 10.

Hand et al. (1978) evaluated each basic dredge type as to its overall potential for hazardous material recovery in four general environmental settings:

i) Land and non-navigable waters: includes dry land beaches, highway or railway drainage ditches, and creeks, streams and rivers not navigable by commercial barge traffic.

ii) Rivers: includes navigable rivers, canals and other freight-carrying waterways having a liner character.

iii) Ports and harbours: includes most tidal and non-tidal harbours and encompasses quiescent waters with heavy shipping traffic and many man-made structures.

iv) Open waters: includes bays, sounds, estuaries, large lakes, coastal ocean waters, high seas and other expanses of water away from intense traffic and port facilities.

Numerical ratings are presented in four matrices, one for each environmental setting. Each dredge type is assigned a numerical score from 0 (worst) to 10 (best) for each of the rating criteria. A weighted average is computed to produce a score for each dredge in each spill setting. The dredge evaluation matrices do not consider the possible influence of chemical-specific considerations nor do they take into account problems of dredged material transport, treatment and disposal.

The individual rating criteria used in the evaluation matrices are:

Job Size Compitibility: The total volume of the contaminated bottom sediments to be dredged and not the spill volume is the prime consideration in each matrix. To properly select a dredge for a specific job, the amount of material to be excavated must be estimated. The dredge chosen must have sufficient production capacity but not so great as to lose cost-effectiveness through overkill.

Solids Content: The solids content refers to the relative amount of settleable solid material contained in a water-sediment slurry. For a given sediment, one dredge type may be capable of yielding denser slurries than another, thereby reducing the amount of material to be handled and water to be treated. Dredges capable of producing the densest material receive the highest score.

TABLE 6

SUMMARY OF DREDGE OPERATING CHARACTERISTICS (Hand et al., 1978; Phillips and Malek, 1984)

Dredge	% Solids in Slurry by Weight^a	Turbidity Caused	Operate in Open Water	Liquid or Solid	Vessel Draft (m)	Production (m^3/h)	Min. Depth (m)	Max. Depth (m)	Wave Height (m)	Max. Lateral Accuracy^i (m)	Vertical Accuracy (m)	Dredging Cost^j ($\$/m^3$)
Dipper	in-situ	high	yes^b	solid	c	23 to 460	0^d	15	0.9^g	0.15	0.6	2.10
Clamshell or Grab	in-situ	high	yes^b	solid	c	23 to 460	0^d	46^e	0.9^{g,h}	0.3	0.6	2.10
Suction	10 to 15%	low	yes^b	both	1.5 to 1.8	19 to 7645	1.5 to 1.8	15 to 18^f	0.9	0.6 to 0.9	0.3	1.95
Dustpan	10 to 20%	avg	no	both	1.5 to 4.3	19 to 7645	1.5 to 4.3	15 to 18^f	0.9	0.6 to 0.9	0.15	1.95
Cutterhead	10 to 20%	avg	yes^b	both	0.9 to 4.3	19 to 7645	0.9 to 4.3	3.6 to 20^f	0.9	0.6 to 0.9	0.3	1.95
Hopper	10 to 20%	avg	yes	both	3.6 to 9.4	382 to 1530	3.0 to 8.5	20^f	2.1	3.0	0.6	1.80
Pneuma	up to 80% of in-situ	low	yes^b	both	c	46 to 300	0^d	46.0	0.9^{g,h}	0.15	0.3	1.40 to 4.00
Hand-held vacuum	5 to 10%	low	yes	both	c	7.6	0^d	30.5	0.9^{g,h}	0.15	-	-
Oozer	up to 80% of in-situ	low	yes	both	-	344 to 500	-	31 to 46	-	0.6 to 0.9	0.3	-
Refresher	30 to 40%	low	yes	both	0.9 to 4.3	150 to 995	6.1	18.3	0.9	0.6 to 0.9	0.3	2.70
Mudcat	10 to 40%	low	no	both	0.5	46 to 115	0.5	4.6	0.3	0.15	0.15	1.95

- - information not available
- a - percent solids could theoretically be zero, but these are normal working ranges
- b - limited operation in open water feasible, depending on hull size and type, and wave height
- c - depends on floating structure; if barge-mounted, approximately 1.5 to 1.8 m
- d - zero if used alongside of waterway; otherwise, draft of vessel will determine
- e - demonstrated depth; theoretically could be used much deeper
- f - with submerged dredge pumps, dredging depths have been increased to 30 m or more
- g - depends on supporting vessel - usually barge-mounted
- h - theoretically unaffected by wave height; digging equipment not rigid
- i - vertical dredging accuracies are generally within 0.3 m
- j - cost values shown are representative of Commencement Bay (U.S. EPA Superfund site, State of Washington) for the cutterhead, bucket and hopper dredges; values for other dredges are derived by relation to conventional equipment; variability may exceed plus or minus a factor of 2 to 3

Notes: - Literature infers that water current hinders dredging operations, but maximum current limitations have not been established; for most dredges, limiting current probably ranges from 3 to 5 knots, with hopper dredges slightly greater, perhaps 7 knots.

TABLE 7 SPILL SCENARIO FOR LAND AND NON-NAVIGABLE WATERS

	Job Size Compatibility*							Overall Potential			
	Small	Medium	Large	Solids Content	Resuspension of Sediments and Contaminants	Debris and Structural Obstacles	Transportation /Mobilization Time	Small Yardage	Medium Yardage	Large Yardage	Notes
	5	5	5	1	2	1	2	NA	NA	NA	NA
Mechanical	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Dipper			(setting normally inaccessible to this type of equipment)								
Clamshell											
Hydraulic	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Cutterhead (and plain suction)			(setting normally inaccessible to this type of equipment)								
Dustpan											
Hopper											
Pneumatic	6	8	6	7	7	7	3	5.8	6.7	5.8	a,b,c
Other											
Mudcat	9	7	2	6	6	4	7	7.4	6.5	4.2	
Handheld Vacuum	5	3	0	2	9	8	8	6.3	5.4	4.0	a,d
Land-based, earth-loading equipment	9	9	9	10	2	8	9	7.7	7.7	7.7	e

* - small < 764.6m^3 (< 1 000 yd^3); medium 764.6 to 152 911 m^3 (1 000 to 200 000 yd^3); large > 152 911 m^3 (> 200 000 yd^3)

NA - not applicable

a - plain suction will be effective only in free flowing sediments such as sands, unconsolidated silty, clayey, or organic sediments, and liquids

b - pneumatic systems which are normally operated in a plain suction mode could be operated with a variety of suction head devices such as augers and cutters

c - equipment can be land-based and/or operated from the shore

d - handheld vacuum will seldom be suitable as a first line recovery device due to extremely limited production capacity. Probably will be most useful for precise cleanup and peripheral operations in situations of small, concentrated well-defined spills; and for cleanup in close quarters

e - includes such equipment as backhoes, front-end loaders, dozers, draglines, and shovels varying in size from small farm tractor mounted to large ship mining equipment

Note: The numerical scores reflected in this table should not be construed as an absolute measure of the dredge's value.

TABLE 8 SPILL SCENARIO FOR A RIVER

	Job Size Compatibility*			Solids Content	Resuspension of Sediments and Contaminants	Dredging Depth Limitation	Vessel Draft Limitation	Debris and Structural Obstacles	Hindrance to Traffic	Current Limitations	Transportation Mobilization Time	Overall Potential			Notes
	Small	Medium	Large									Small Yardage	Medium Yardage	Large Yardage	
Weighting Factor	6	6	6	1	3	1	2	2	1	1	2	NA	NA	NA	NA
Mechanical															
Dipper	7	5	1	10	1	4	8	7	7	6	4	5.8	5.2	3.9	a,b,g
Clamshell	8	6	2	10	1	10	8	9	7	6	4	6.6	6.0	4.7	a,b,g
Hydraulic															
Cutterhead (and Plain Suction)	3	7	9	5	5	6	7	3	3	7	2	4.1	5.4	6.0	c,e,f
Dustpan	3	7	8	5	5	6	7	3	3	7	2	4.1	5.4	5.7	f
Hopper	3	7	7	5	5	6	2	1	9	9	4	4.0	5.3	5.3	f
Pneumatic	6	7	4	7	7	10	7	9	3	6	5	6.6	6.9	5.9	c,d,g
Other															
Mudcat	9	5	2	6	6	3	9	4	5	4	8	7.0	5.7	4.7	i
Handheld Vacuum	5	1	0	2	9	6	10	10	6	1	9	6.8	5.6	5.3	c,h

* - small < 764.6 m^3 (< 1 000 yd^3); medium 764.6 to 152 911 m^3 (1 000 to 200 000 yd^3); large > 152 911 m^3 (> 200 000 yd^3)

a - can only be used for a solid contaminant unless it is known that a liquid contaminant is adsorbed in the sediment

b - pure mechanical devices will be relatively ineffective on hard rock or hardpan clay sediments

c - plain suction will be effective only in free flowing sediments such as sands, unconsolidated silty, clayey, or organic sediments, and liquids

d - pneumatic systems which are normally operated in a plain suction mode could be operated with a variety of suction head devices such as augers and cutters

e - cutterheads should be turned off when operating in a rock or hardpan bottom to avoid unnecessary dispersion of contaminant and/or damage to dredging equipment

f - dredging depths can be effectively increased with the addition of auxiliary booster pumps at the suction head

g - equipment can be land-based and/or operated from the shore

h - handheld vacuum will seldom be suitable as a first line recovery device due to extremely limited production capacity; probably will be most useful for precise cleanup and peripheral operations; in situations of small, concentrated well-defined spills; and for cleanup in close quarters

i - mudcat cannot be used in open water situations due to severe depth and wave height limitations but probably would be most effective in small, non-navigable streams

Note: The numerical scores reflected in this table should not be construed as an absolute measure of the dredge's value.

TABLE 9 SPILL SCENARIO FOR PORTS AND HARBOURS

	Job Size Compatibility*										Overall Potential			
	Small	Medium	Large	Solids Contents	Resuspension of Sediments and Contaminants	Dredging Depth Limitation	Vessel Draft Limitation	Debris and structural Obstacles	Hindrance to Traffic	Transportation Mobilization Time	Small Yardage	Medium Yardage	Large Yardage	Notes
Weighting Factor	5	5	5	1	1	1	1	2	1	1	NA	NA	NA	NA
Mechanical														
Dipper	7	5	1	10	1	4	9	7	8	5	6.6	5.9	4.3	a,b,g
Clamshell	8	6	1	10	1	10	9	9	8	5	7.8	7.0	5.1	a,b,g
Hydraulic														
Cutterhead (and Plain Suction)	3	7	9	5	5	6	8	3	4	3	4.0	5.5	6.3	c,e,f
Dustpan	3	7	8	5	5	6	8	3	4	3	4.0	5.5	5.9	f
Hopper	3	7	7	5	5	6	5	1	9	4	3.9	5.5	5.5	f
Pneumatic	6	7	4	7	7	10	8	9	4	5	6.9	7.2	6.1	c,d,g
Other														
Mudcat	9	5	2	6	6	1	9	4	5	8	6.8	5.2	4.1	i
Handheld Vacuum	5	1	0	2	9	6	10	10	7	9	6.8	5.2	4.9	c,h

* - small < 764.6 m^3 (< 1 000 yd^3); medium 764.6 to 152 911 m^3 (1 000 to 200 000 yd^3); large > 152 911 m^3 (> 200 000 yd^3)
a - can only be used for a solid contaminant unless it is known that a liquid contaminant is adsorbed in the sediment
b - pure mechanical devices will be relatively ineffective on hard rock or hardpan clay sediments
c - plain suction will be effective only in free flowing sediments such as sands, unconsolidated silty, clayey, or organic sediments, and liquids
d - pneumatic systems which are normally operated in a plain suction mode could be operated with a variety of suction head devices such as augers and cutters
e - cutterheads should be turned off when operating in a rock or hardpan bottom to avoid unnecessary dispersion of contaminant and/or damage to dredging equipment
f - dredging depths can be effectively increased with the addition of auxiliary booster pumps at the suction head
g - equipment can be land-based and/or operated from the shore
h - handheld vacuum will seldom be suitable as a first line recovery device due to extremely limited production capacity; probably will be most useful for precise cleanup and peripheral operations; in situations of small, cencentrated well-defined spills; and for cleanup in close quarters
i - mudcat cannot be used in open water situations due to severe depth and wave height limitations but probably would be most effective in small, non-navigable streams

Note: The numerical scores reflected in this table should not be construed as an absolute measure of the dredge's value.

TABLE 10 SPILL SCENARIO FOR OPEN WATERS

	Job Size Compatibility*			Solids Content	Resuspension of Sediments and Contaminants	Dredging Depth Limitation	Hindrance to Traffic	Wave Height	Transportation Mobilization Time	Overall Potential			Notes
	Small	Medium	Large							Small Yardage	Medium Yardage	Large Yardage	
Weighting Factor	8	8	8	1	1	4	1	1	4	NA	NA	NA	NA
Mechanical													
Dipper	7	5	1	10	1	4	4	4	4	5.4	4.6	3.0	a,b
Clamshell	8	6	1	10	1	10	4	5	4	7.2	6.4	4.4	a,b
Hydraulic													
Cutterhead (and Plain Suction)	3	7	9	5	5	6	4	4	3	4.1	5.7	6.5	c,e,f,i
Dustpan	3	7	8	5	5	6	4	4	3	4.1	5.7	6.1	f
Hopper	3	7	7	5	5	6	9	10	6	5.7	7.3	7.3	f,i
Pneumatic	6	7	4	7	7	10	4	5	5	6.6	7.0	5.8	c,d
Others													
Mudcat	9	5	2	6	6	1	4	1	8	5.2	3.6	2.4	c,g
Handheld Vacuum	5	1	0	2	9	6	7	8	9	6.2	4.6	4.2	c,g

* - small < 764.6 m^3 (< 1 000 yd^3); medium 764.6 to 152 911 m^3 (1 000 to 200 000 yd^3); large > 152 911 m^3 (> 200 000 yd^3)
a - can only be used for a solid contaminant unless it is known that a liquid contaminant is adsorbed on the sediment
b - pure mechanical devices will be relatively ineffective on hard rock or hardpan clay sediments
c - plain suction will be effective only in free flowing sediments such as sand and liquids
d - pneumatic systems which are normally operated in a plain suction mode could be operated with a variety of suction head devices such as augers and cutters
e - cutterheads should be turned off when operating in a rock or hardpan bottom to avoid unnecessary dispersion of contaminant and/or damage to dredging equipment
f - dredging depths can be effectively increased with the addition of auxiliary booster pumps at the suction head
g - handheld vacuum will seldom be suitable as a first line recovery device due to extremely limited production capacity; probably will be most useful for precise cleanup and peripheral operations; in situations of small, concentrated well-defined spills; and for cleanup in close quarters
h - mudcat cannot be used in open water situations due to severe depth and wave height limitations but probably would be most effective in small, non-navigable streams
i - swell compensators can increase ability to operate in higher wave environment

Note: The numerical scores reflected in this table should not be construed as an absolute measure of the dredge's value.

Resuspension of Sediments and Contaminants: Ratings are based on qualitative observations and relative comparisons among various dredge types. The relative weight given to this criterion depends on the degree of concern over hazardous material resuspension.

Dredging Depth Limitation: At a spill site, the water depth will allow the use of a dredge or preclude its use. The importance of water depth as a consideration in the overall score increases in the settings where the water depths may limit one or more types of dredges.

Vessel Draft Limitation: Sometimes the water in which the dredging operation will take place will be too shallow to accommodate the vessel mounting the dredge. Draft limitations are weighted as to their importance in each particular environmental setting.

Debris and Structural Obstacles: This criterion addresses the effects of debris and man-made structures on the proper and efficient operation of the various dredge types. Individual dredges are scored according to their ability to work normally around and among obstacles.

Hindrance to Traffic: It is assumed that in the event of a spill recovery operation, a temporary stoppage of shipping traffic will occur; however, some dredge types are more obstructive than others. This fact is accounted for in the overall scores.

Wave Height: Wave height is a major factor in discriminating among dredges in the open-water setting, and therefore has a high weighting factor in this setting.

Current Limitations: Precise information on the sensitivity of dredging vessels to strong currents is not available. The limiting current for barge-mounted systems is in the 3 to 5 knot range and hopper dredges can operate in somewhat faster currents. Mudcat dredges are more sensitive to currents than barge-mounted dredges; divers wielding suction hoses would be the most limited by currents.

Current cannot be ignored where it has potential to influence the operation yet in comparison to other criteria it is relatively minor. In the land and non-navigable stream, open water and port and harbours setting, current is not considered an important enough consideration to be included in the dredge selection process.

Transportation/Mobilization Time: This factor incorporates several components such as: ease of transport over long distances; ease of moving to spill site; the probable need for custom modification; the likelihood of dredge type being available and in suitable proximity; and the time required for contract negotiations. The actual scores are based on the need for urgency in a given setting.

2.3 Environmental Considerations

2.3.1 Environmental Effects. Investigations conducted by the United States Army Engineers Waterways Experiment Station have studied the environmental effects of dredging and disposal operations (U.S. Army, 1975a,b; 1976; 1977). Documented effects include increases in turbidity, suspended solids concentration and biochemical oxygen demand, and decreases in concentration of dissolved oxygen and distribution of benthic organisms. Less direct effects are alterations in bottom topography due to changes in benthic communities and current flow patterns. Potential temporal effects of dredging are presented in Table 11.

TABLE 11 POTENTIAL EFFECTS OF DREDGING OPERATIONS (Hand et al., 1978)

	Adverse	Beneficial	Short Term	Long Term
Decrease				
Dissolved oxygen	x		x	
Benthic organisms	x		x	x
Increase				
BOD	x		x	
Turbidity	x		x	
Suspended solids	x		x	
Toxic substances	x		x	x
Heavy metals	x		x	
Change				
Sediment-H_2O interface	x	x	x	x
Sediment flow patterns	x	x	x	x
Bottom geometry	x	x	x	x
Benthic community	x	x	x	x

The dredge used and the type of sediment affect the degree of adverse impact. Dredges creating the greatest turbidity cause the most contaminant resuspension and pose the greatest threat to the aquatic organisms present.

2.3.2 **Turbidity Control.** Turbidity control is an important consideration in the dredging of heavily contaminated sediments. Control can be achieved by the use of improved designs of dredging heads to minimize material resuspension or curtain barriers to contain the turbidity plume.

A special dredging head, developed in Japan and known as "Cleanup", is used with standard hydraulic suction dredges for the cleanup of contaminated sediments with minimum material resuspension and optimum dredging accuracy. The suction head is completely enclosed by an articulated box that allows water to be entrained and mixed from one direction only. It also features a trap that captures noxious gases released during sediment disturbance, and is highly instrumented to ensure a constant cutting depth and slurry density. Evaluations have shown that the turbidity and chemical oxygen demand in close proximity to the cleanup head are virtually the same as that of the undisturbed water. Dredging head specifications were unavailable at the time of writing.

Silt curtains are often used for turbidity control in dredging projects and construction activities such as pile driving, and airport and highway construction. They consist of a boom supported fabric barrier ballasted at the bottom and backed by a tensioning line approximately one quarter to one third of the way to the skirt bottom (Figure 13). There is no theoretical limit to the curtain length though local environmental conditions and handling characteristics would determine the length on a situation-specific basis. Curtain lengths in excess of 600 m have been reported. Curtain drafts have been reported up to 6 m, though the practical maximum is generally 3 m. Typical deployment configurations are illustrated in Figure 14. It is important to remember that as the curtain does not extend to the bottom of the waterway, fines that have not settled out will be carried under the curtain by currents. These curtains are effective for surface turbidity control at current speeds up to 0.5 knots only. Due to these limitations, the best application for silt curtains is in calm, protected, and shallow water.

2.3.3 Turbidity and Contaminant Resuspension Studies. The U.S. Army Engineer Waterways Experiment Station (WES) has been conducting evaluations of sediment resuspension caused by cutterhead, dustpan, clamshell and hopper dredges under the Improvement of Operational and Maintenance Techniques (IOMT) Research Program (Hayes et al., 1984).

Cutterhead. In previous work performed by Japanese researchers on the cutterhead dredge, it was concluded that production, efficiency, and sediment resuspension are related to the depth of cut, swing speed, and cutter rotational speed. In July of 1983, the WES conducted a cutterhead dredging field study in the Savannah River, Virginia. This study confirmed the Japanese findings and determined that the swing speed is the most significant factor for partial cuts while the cutter tip speed has a greater impact on sediment resuspension for full cuts. Research indicates that the turbidity plume may extend 300 m downstream at the surface and 450 m near the bottom.

At a distance from the dredge (i.e., > 6 m), the suspended sediment level appears to be influenced more by the current velocity than by the action of the dredge. Higher current velocities magnify the effects of the dredging operation by creating higher suspended solids levels near the bottom and further up into the water column.

Clamshell. Increased turbidity associated with the clamshell dredge is caused mostly by the impact, penetration and withdrawal of the bucket from the bottom

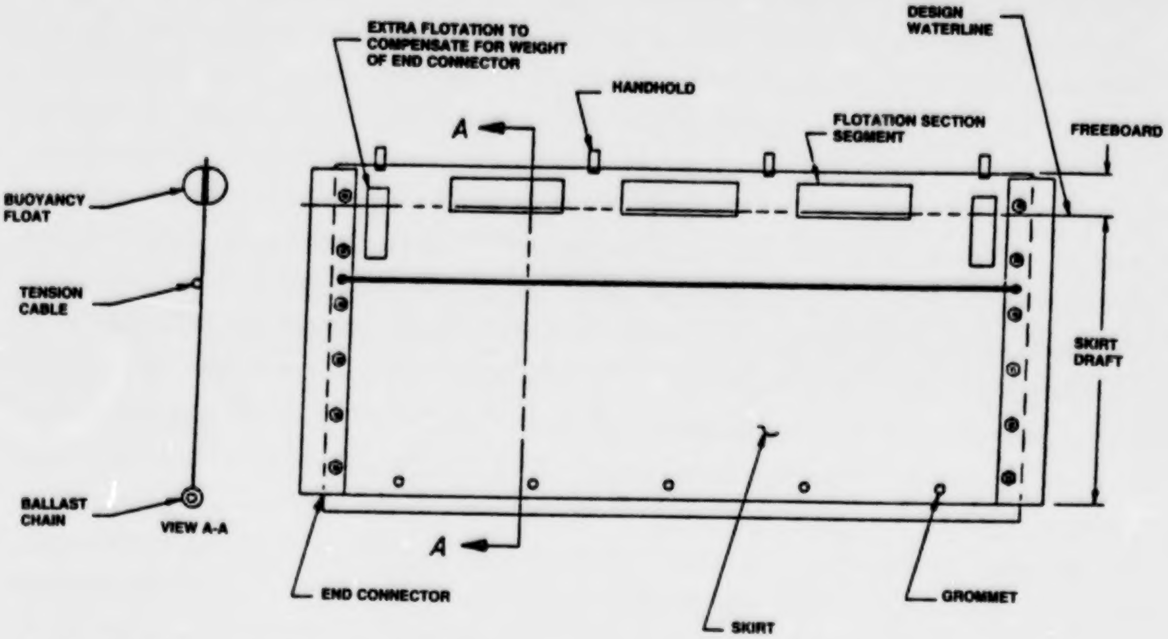


FIGURE 13 TYPICAL SILT CURTAIN SECTION (Hand et al., 1978)

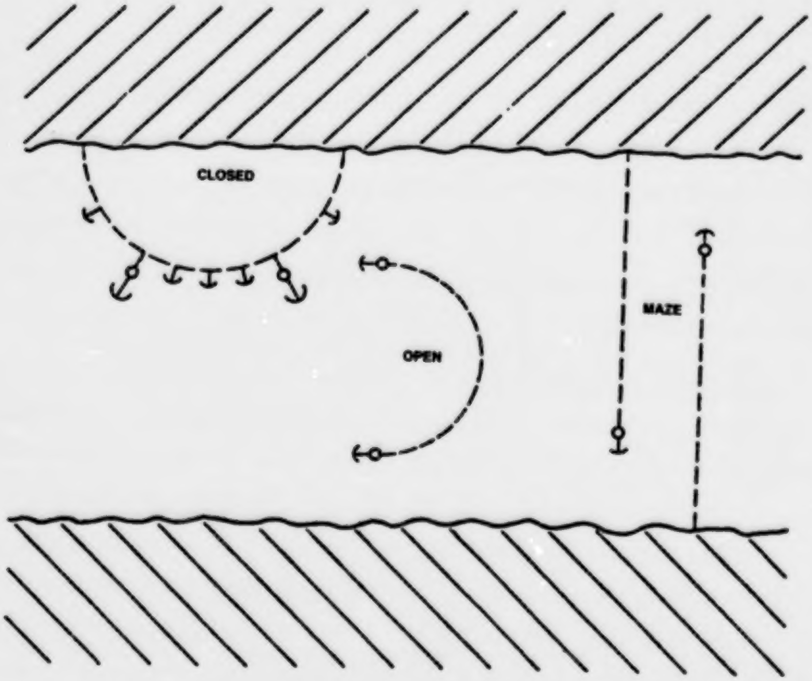


FIGURE 14 TYPICAL DEPLOYMENT CONFIGURATIONS (Hand et al., 1978)

sediments. Additional material loss occurs as the bucket is pulled through the water and when the bucket breaks the surface. Material loss is also influenced by the sediment properties, the hoisting speed and the fit and condition of the bucket.

The Port and Harbour Institute of Japan has developed a watertight bucket that generates 30 to 70% less turbidity than the standard bucket. Comparative evaluations performed in the St. Johns River, Florida, determined that the enclosed bucket provides a 35 to 45% turbidity reduction in the upper water column. The enclosed bucket does nothing to eliminate the turbidity in the lower water column associated with the penetration, digging and withdrawal actions. The advantage of the watertight clamshell lies in its ability to reduce losses as the bucket moves through the water.

Hopper. Field data indicates that the turbidity generated by a hopper dredge is primarily caused by overflow. The plume in the immediate vicinity of the dredge is generated by the overflow process; a near-bottom plume is generated by draghead resuspension. The surface plume can reach 60 m in width and 1200 m in length with suspended solids reaching 857 mg/L, 30 m behind the dredge (Hayes et al., 1984). The near bottom plume can obtain dimensions of 120 x 2600 m. A study of the plume generated by the suction draghead only revealed no turbidity at the surface or mid-depth. The plume at the bottom reached 60 x 1100 m with the highest turbidity level being 70 mg/L.

Mudcat. The U.S. EPA evaluations (Nawrocki, 1976) have included a turbidity study of the Mudcat dredge. The retractable mudshield over the auger is positioned to minimize the mixing of the bottom sediments and the surrounding water. During normal dredging operations, it was observed that the turbidity plume was confined to within 4.5 to 6.0 m of the dredge. During simulated failure, the plume of suspended material stayed within 7.6 m of the dredge.

Oozer Dredge and Cleanup Head. Japanese researchers undertook an evaluation of the turbidity associated with the Oozer dredge and the Cleanup head while dredging contaminated bottom sediments in Osaka Bay (Koba and Shiba, 1981). It was observed that the resuspension was caused primarily by the movement of the suction mouth. By varying the swing speed it was found that contamination was virtually eliminated when set at 6 to 7 m/min. At 1.5 m from the bottom, almost all measured suspended solids were within the range of 5 to 10 mg/L, which is within the mean suspended solids background value of 9 to 10 mg/L.

To date, little research has been conducted comparing the turbidity generated by various dredges. The Japanese determined that the hopper and cutterhead dredges have similar resuspension potential in clay sediments. The clamshell was found to produce about 2-1/2 times as much resuspension. The Oozer dredge produces the least sediment resuspension.

Evaluations conducted under the IOMT determined that for the upper water column, the cutterhead and hopper dredge (without overflow) produced less sediment resuspension. The clamshell and hopper dredge (with overflow) produce decidedly more resuspension. With the latter two, turbidity can be reduced by use of the enclosed bucket and not pumping past overflow.

Under the IOMT program, the WES is continuing to study the problem of limiting the environmental impact of dredging contaminated sediments. Areas to be addressed include the effectiveness of special purpose dredges in limiting sediment resuspension as compared with conventional dredges, and the combinations of operational and equipment modifications that are most cost-effective in reducing suspended sediments.

2.4 Recommendations for Dredge Use During Spill Cleanup

A survey of the literature reveals several recommendations for dredge clean-up:

- Dredging may cause resuspension and additional dispersion of the contaminant. In flowing water bodies, redeposition of the contaminant from upstream will be minimized by initiating clean-up at the furthest upstream point and proceeding downstream.
- In nonflowing watercourses the spread of material will be minimized by initiating cleanup at the area where the heaviest contamination has been detected.
- On-scene analytical capabilities appropriate to the spilled material should be maintained to determine the presence of contaminant in the dredged material. This will prevent over-dredging and under-dredging of the area.
- Several incident-specific parameters should be determined before cleanup is initiated:
  - the safe residual concentration of the chemical,
  - its persistence in the environment, and
  - the location of the spill and the uses of the affected waterbody.
- Large-scale dredging in small streams should only be used in special cases where flow, terrain and other circumstances dictate it to be the only feasible method;

permanent scars on the streambank or expensive restorative landscaping are therefore avoided where possible.

2.4.1 Limitations and Availability. The applicability of dredges and dredging techniques to hazardous chemical spill cleanup are limited by various factors:

- Dredging alone can seldom be expected to accomplish the total recovery of spilled chemicals, and should be considered in combination with other measures such as in-situ chemical treatment or burial.
- Depth, draft limitations and environmental constraints limit the dredge types appropriate to specific environmental settings.
- The location and availability of specific dredge types may result in long lead times.
- Dredging may result in resuspension and additional dispersion of the contaminant.
- Dredging may cause adverse effects such as increases in suspended solids, turbidity and BOD as well as decreases in dissolved oxygen and distribution of benthic organisms.
- Dredged slurries are generally 80 to 90% water, resulting in the handling and treatment of large volumes of water.

As stated earlier, dredges do not normally come in standard models but are designed for a specific job. An inventory of the Canadian private dredging fleet is summarized in Table 12. Addresses of selected dredge manufacturers can be found in Appendix A.

TABLE 12 CANADIAN PRIVATE DREDGE FLEET INVENTORY: REGIONAL DISTRIBUTION (WODCON, 1985)

Dredge Type	Western Canada	Prairies	Ontario	Quebec	Atlantic Canada
Suction Hopper	2	1	2		
Cutter Suction	15	2	18	3	3
Suction	2	1	1	2	
Bucket Suction	1				
Bucket Ladder					1
Grab/Clamshell	15		30	1	5
Bucket Dipper			8		1
Grab Hopper			1		
Bucket Backhoe	3		4		1

2.4.2 Dredging Costs. The cost of dredging per unit volume is extremely variable and is a function of location and job size, substrate type, depth, proximity and type of disposal area, etc. Average dredging costs of \$1.96/m^3 are quoted in the World Dredging and Marine Construction Journal (January, 1985). Dredging costs as reported by Phillips and Malek (1984) vary from \$1.39/m^3 to \$3.05/m^3 with an average of \$1.63/m^3.

3 CONTAINMENT

Containment involves the use of a physical barrier to limit dispersion and permit in-water treatment of the spilled hazardous material. With containment, chemicals can be more safely added and reaction rates better controlled. The efficiency and cost-effectiveness depend primarily on the ability to contain spills successfully. The effectiveness of the containment measure depends on the nature of the spill, the size of the contaminated waterbody, the mode of dispersion, and the rapidity of response.

Typical containment devices for sunken chemical spills in water include dykes, trenches, curtain barriers, and diversion systems. Descriptions and limitations of these techniques follow.

3.1 In-water and Submerged Dykes

In-water and submerged dykes can be used to contain the spilled material before effective collection can be initiated. These dykes would prevent dispersion of the material and permit efficient use of the covering material or treatment technique. The literature does not contain information on the application of dykes to spills of hazardous materials.

In-water dykes are generally constructed of granular material using dredging or earthmoving equipment. They often have sloped embankments which are constructed either in the water or directly bordering lowland areas and islands. Studies on dykes used to control mudflows indicated that the dyke must be twice as high as that of the mudflow to impede its progress (White, 1966). Use of dykes has been limited and has generally been undertaken in depths less than 10 m. Retaining dykes are confined to quiescent nearshore or shallow water areas of rivers and harbours, possibly surrounded on one or more sides by natural barriers. The feasibility of dykes for spill control diminishes as the spill becomes larger; mobilization and construction time will increase, reducing the effectiveness of the dyke as an emergency response procedure. Because of its impact on the environment and obstruction to free use of waterways, the dyking operation for large spills could become a greater problem than the spill itself.

An emergency dyke constructed of hydraulic fill would cost \$5.25/m^3 (1984 U.S.\$). A 6-m high dyke with a 4:1 slope would cost at least \$750.00 per linear metre. Engineer's fees and contingency costs are extra.

3.2 Trenches

Trenches, particularly in rivers or other bodies of water with predictable currents, may be useful for trapping insoluble sinking chemicals.

Experiments using liquid ethylene dichloride indicate that gravity separation using trenches is a feasible method of controlling hazardous materials spills (Pilié et al., 1975). Approximately 85% of the original volume was collected in a simulated spill at low flowrates down a 2% grade. Simulations at high flows (unspecified) revealed no change in the collection process. The experimental configuration is illustrated in Figure 15.

The type and amount of covering material, frequency of covering activity, and local topography and bottom currents must be considered when placing and sizing trenches. In locations with unidirectional flow a downstream trench would be advantageous, while in cases of varying or random flow, an enclosed circle would be the most useful configuration.

Natural depressions would probably not be successful as containment areas as the forces that created the depression would also remove the spilled material that might collect there.

Dredging equipment such as land- or water-based clamshells, draglines and hydraulic or suction dredges are necessary for submerged trench construction. The choice of dredging device is dictated by the locale and characteristics of the spill area. Non-navigable waters could be handled by land-based clamshells or hand-held suction dredges. Hydraulic dredges could be utilized for larger spills in deep water.

Unterberg et al. (1984) indicated that excavation of a submerged trench is only practical in water depths less than 15 m. Wind, wave action and currents will also limit dredging operations.

The costs for submerged trench construction has been estimated to be \$6.50 to \$20/m^3 (1984, U.S.\$).

3.3 Diversion Systems

Spills into small streams and reservoirs can sometimes be contained by isolating a section and diverting the flow around it. Waterbodies that fall into this category generally have too high a flow to allow stoppage by damming, and too low a flow to produce rapid dilution and dispersion of contaminants.

Three cases of spill cleanup using stream diversion have been reported. In the first case, the low flow in the creek (0.22 m^3/h) allowed diversion with dams and a long length of flexible tubing laid in the streambed. This technique eliminated the use of a

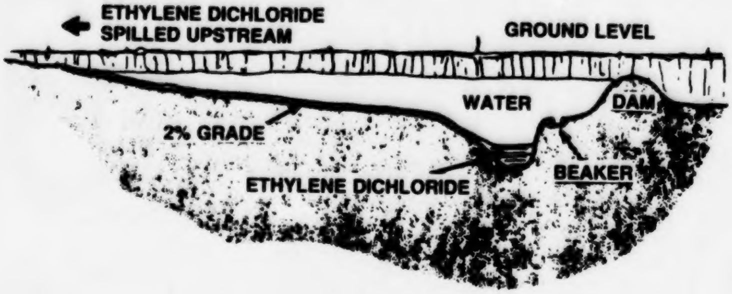


FIGURE 15 TRENCH CONSTRUCTION FOR TRAPPING SINKING SPILLS (Pilié et al., 1975)

pump but the tube interfered with the treatment of the isolated section. In the second case a stream was isolated from a reservoir by using dams and two 9.5 m^3/min. pumping systems to bypass the flow. In the third case, diversion was achieved with the EPA mobile stream diversion system.

These methods are only appropriate for streams and reservoirs with relatively low flow rates. The infrequent need for this approach resulted in the removal of the mobile stream diversion system from use by the U.S. EPA.

3.4 Hazardous Material Containment Barrier

A hazardous material containment barrier deployed to encircle the spill location was developed for the U.S. EPA to contain chemical spills in water (Figure 16). Individual barrier units consist of a 61-m long section of flexible, fibre-reinforced plastic. Buoyancy is provided by an inflatable flotation collar. The weighted bottom of the boom forms a seal along the bed of the waterway, and is secured by explosive anchors.

Deployment of the barrier requires a minimum crew of five, one or two outboard-powered boats, and portable air compressors and an integrated water pump (Hand et al., 1978). The system was designed to be transported in a small truck or helicopter. During trials in Sugar Grove, West Virginia, the system was deployed in six hours.

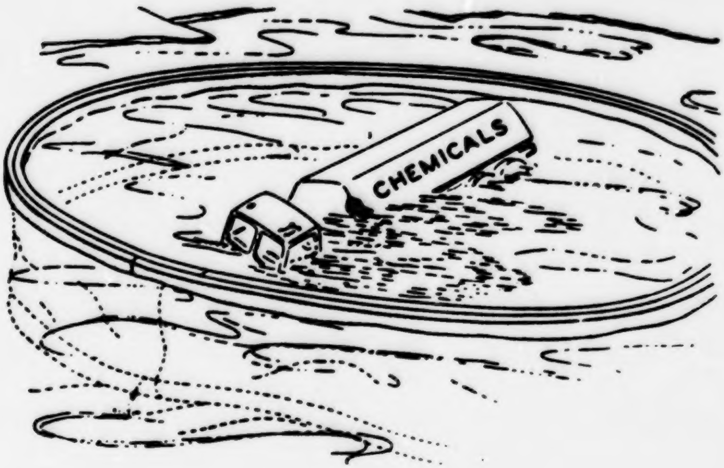


FIGURE 16 DEPLOYMENT OF HAZARDOUS MATERIAL CONTAINMENT BARRIER (Hand et al., 1978)

The most significant problem associated with the use of this system is water currents; it is effective only with currents <1 knot, winds <40 knots, and waves <2 m. Difficulty in deployment has been experienced with currents as low as 0.75 knots. This unit is limited to water depths of eight metres; it has never been tested in open waters; and problems have been experienced with maintaining the bottom seal. There is a time lag before deployment and the barrier should probably be confined to spills in quiescent waters.

This system has been developed to the prototype stage only. Plans by the U.S. EPA do not include development of a commercial product.

The basic module and mooring tackle was quoted at $65 000 (1978 U.S.$). Air compressors, inflatable rafts, and ancillary equipment must be purchased separately.

4 COVERING AND SOLIDIFICATION/CEMENTATION

Contaminated sediments may be chemically and biologically isolated from the water column by covering or capping with a layer of clean material (Figure 17). Such disposal practices may be environmentally superior to on-land disposal and, as such, are gaining acceptance as an extremely useful disposal alternative (Shields and Montgomery, 1984). Burial can be achieved either at the spill site or in a less environmentally sensitive location. In-situ burial techniques have been suggested as potential responses to spills of hazardous sinking chemicals in water; however, this may seldom be the most desirable response. Although Unterberg et al. (1984) indicate that under no circumstances should in-situ burial be considered as a permanent response, Hand et al. (1978) state that in-situ burial of certain chemicals (Table 13) may be appropriate in the following situations:

- as a temporary mitigating measure to retard dispersion or reduce the hazard until removal can begin;
- as a final step to isolate any residual contaminated sediment; and
- as a sole response when recovery is not feasible or when the material is harmless (or nearly so).

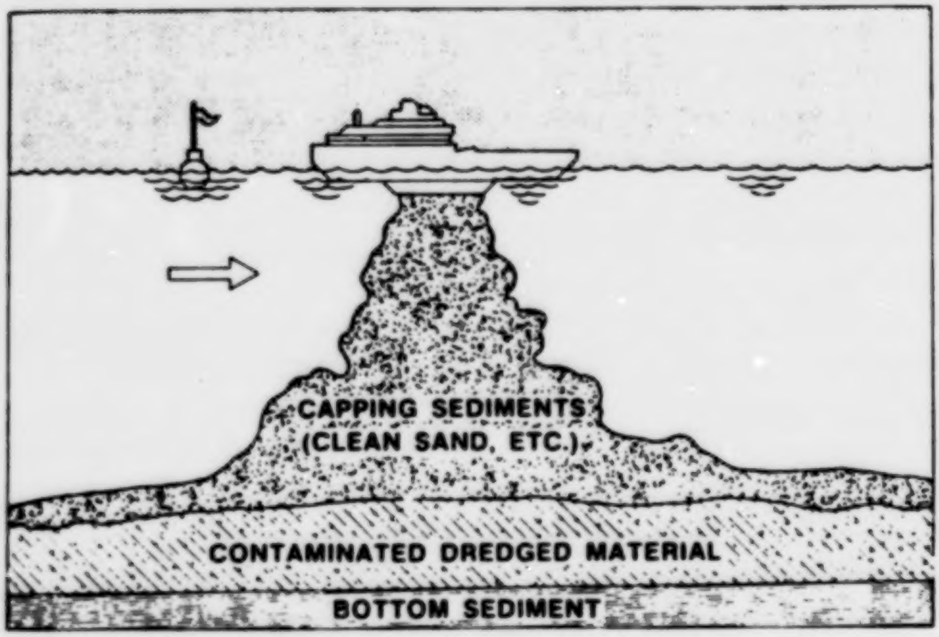


FIGURE 17 HOPPER DREDGE PLACING CAP MATERIAL
(Shields and Montgomery, 1984)

TABLE 13 CHEMICALS AND MATERIALS AMENABLE TO BURIAL (Hand et al., 1978)

Aluminum fluoride
Asphalt
Barium carbonate
Calcium hydroxide
Calcium fluoride
Lead arsenate
Phosphorus, white
Phosphorus, red
Sulphur

Chemicals listed in Table 13 were considered to be harmless or offered an even greater threat if recovery was attempted. The London Dumping Convention, of which Canada is a signatory, has accepted capping of contaminated sediments in open-water disposal sites, subject to careful monitoring and research (Shields and Montgomery, 1984). It should be noted that burial of liquids may be considered inappropriate due to their tendency to disperse when contacted by covering material.

There are three categories of materials that can be used to cover submerged spills of hazardous material: inert, chemically active, and sealing agents. Each category varies in the nature of the material, its ability to retard downward movement, its susceptibility to scour, and its potential impacts on biota. The characteristics of existing capped disposal sites are summarized in Table 14.

TABLE 14 CHARACTERISTICS OF EXISTING CAPPED DISPOSAL SITES (Shields and Montgomery, 1984)

Location	Capping Site	Volume of Contaminated Material (m^3)	Volume of Cap (m^3)	Thickness of Cap (m)	Dredge	Placement	Positioning
Rotterdam Harbour, The Netherlands	Excavated	1 500 000			Hydraulic Suction	Submerged Diffuser	Surveying Instruments
Duwamish Waterway Seattle, WA	Subaqueous Depression (20-m deep)	680	765	0.6	Clamshell	Scow	Surveying Instruments
Hiroshima Bay, Japan	Contaminated bottom sediments covered with clean sand	No dredging	25 600 sand	0.3 to 0.5		Tremie Tube and Sand Spreader	
Central Long Island Sound	Offshore 20-m deep	37 800	76 000 silt	4.0	Clamshell	Scow	buoy
Central Long Island Sound	Offshore 20-m deep	26 000	84 000 sand	3.5	Clamshell and Hopper	Scow and Hopper	buoy
Central Long Island Sound	Offshore 20-m deep	16 000	Silt and sand		Clamshell	Scow	buoy
New York Bight	Offshore 25-m deep	382 000	1 362 000		Clamshell	Scow	buoy
Porpoise Harbour Prince Rupert, B.C.	Inside loading dock 5-m deep	25 000	Hog fuel leachate and rock 100 000		N/A	From shore	N/K

N/A - not applicable

N/K - not known

4.1 Inert Covering Materials

To date, the capping of contaminated sediments has been done almost exclusively with inert materials (Shields and Montgomery, 1984). Inert covering materials include clays, sand, and diatomaceous earth; a more comprehensive list is presented in Table 15.

The most important parameter influencing the success of a covering material is its ability to resist scour and erosion. The rate and extent of scour will depend on particle characteristics (i.e., size, uniformity, shape, size distribution), cohesiveness, and the degree of consolidation. A qualitative guide to the erosion potential of various inert coverings is presented in Table 16. Fine sands are generally more susceptible to erosion than are cohesive materials or coarse sands.

The degree of consolidation has a significant effect on the ease with which fine-grained particles erode. For a cap to remain unbroken and the two layers of sediment to consolidate, the covering material must be more dense than the bottom sediments, and the shear stress along the interface between the two layers must exceed the strength of the deposit (Shields and Montgomery, 1984). Monitoring of the Stamford/Newhaven capping site showed that, in determining the stability of the cover, stress created under storm wave conditions is more important than the depth of the spoil surface, the strength of the currents, or the cohesive nature of the sediment.

The permeability of a material is a good indicator of its ability to retard leaching. The greater the grain size, the greater the permeability and therefore the greater the leaching. Sands have a high permeability and therefore a low resistance to leaching. Some specific clays having a very low permeability can successfully hinder leaching. The absorptive and ion-exchange capacities of the covering material also influence its ability to retard leaching. The ability of clays to physically/chemically "tie-up" various organics and metals increases its desirability as a covering material. The degree of coverage necessary to inhibit diffusion to the water column has not been determined.

When selecting inert capping materials and designing the cap thickness, site-specific biological populations should be considered. The biota likely to recolonize the site will prefer material that is compatible with the natural bottom sediments. A sand

TABLE 15 INERT COVERING MATERIALS (Robinson, 1979)

Coarse-grained	Fine-grained
Gravel	Kaolin clay
Sand	Bentonite clay
Crushed stone	Fuller's earth clay
Crushed glass	Ball clay
	Fire clay
	Miscellaneous clays (local)
	Diatomaceous earth/filter aid

TABLE 16 APPROXIMATE EROSION VELOCITIES FOR VARIOUS INERT MATERIALS (adapted from Robinson, 1979)

Material	Approximate range of erosion velocity (cm/s)
coarse sand/gravel	40 to 300
medium sand	20 to 40
fine sand	20
silt	
consolidated	30 to 70
unconsolidated	9 to 20
clay	
consolidated	50 to 300
unconsolidated	6 to 15

cap attracts suspension-feeding organisms that are not deep burrowers, while a fine-grained cap attracts deep-burrowing feeders. To discourage recolonization and thereby preclude re-exposure of burrowing organisms, it may be desirable to use a sand cap even when it is incompatible. Using depths greater than the burrowing ability of the local organisms will also aid in preventing re-exposure. To inhibit leaching as a result of biological activity, a 1-m cover is generally adequate for protected nearshore waters; however, site-specific studies should be done to evaluate the erosion potential and biological populations.

Capping may be inappropriate for liquids due to their tendency to disperse when contacted by covering material. No chemical alteration occurs; therefore, a threat to the environment exists if erosion causes re-exposure. The depth of coverage required has not been determined and turbidity and sediment resuspension may occur during the overlaying process.

Inert covering materials can be readily obtained by dredging with existing equipment. It may be necessary, however, to modify existing equipment before effective deposition of the cover can be achieved.

Costs of capping are a function of the availability of the covering material. If dredge spoil is available either from the capping project or another nearby project, proper management can produce a capped deposit at very little expense. If dredging must be done solely for the capping material, costs increase substantially.

The Stamford/Newhaven operation cost approximately \$140 000 to cover 30 000 m^3 of contaminated material using a hopper dredge; estimated cost of the cover material was \$1.83/m^3 (Phillips and Malek, 1984).

4.2 Active Covering Materials

Active covering materials react with the spilled chemical to neutralize it or otherwise reduce its inherent toxicity. As most active materials are fine-grained, they are usually combined with an inert material that acts as a stabilizer to reduce the possibility of scour and erosion. Similarly, a layer of inert material could also be added, as a mixture or subsequent layer, to reduce permeability and retard leaching.

Mixing of the two substances can be achieved on land, in a barge, or through slurry injection into a pipeline discharge. As there are no universal covering agents, each spill must be evaluated on a case-by-case basis.

Effects on biota may eliminate several potential active covering agents from use. Careful placement is necessary as misplacement could be detrimental to some organisms that are out of the spill zone itself.

The choice of active covering material is made on the basis of its ability to reduce the toxicity of the spilled material under specific environmental conditions. A list of typical active materials is presented in Table 17. Recommendations for specific chemicals are given in Table 18. Selected agents, their cost, applications and specific gravity are listed in Table 19.

TABLE 17 ACTIVE COVERING MATERIALS (Robinson, 1979)

Covering Material	Active Agent(s) or Mechanism
Scrap iron	Iron oxide absorption
Sulphide ores - pyrite	Iron, sulphide
Diatomaceous earth	Adsoption
Manganese dioxide	Adsorption
Proteinaceous wastes	Sulphide
Wool	
Chicken feathers	
Xanthates	
Carbon compounds	Adsorption (especially organics)
Activated carbon	
Lamp black	
Bone char	
Charcoal	
Calcium carbonates	Carbonate, acid neutralization
Limestone	
Lime	
Chalk	
Stucco	
Spent tannery lime	
Gypsum (calcium sulphate)	Sulphate
Sulphur	Sulphur
Potassium permanganate	Oxidizing agent
Alum (aluminum oxide)	Adsorption
Ferric sulphate	Iron, sulphate
Commercial ion exchangers	Ion exchange

There are some limitations to using active agents: they cost more than inert covering materials; re-exposure due to erosion may occur; and their use may have detrimental effects on biota, which have not as yet been determined.

Active agents are readily available from several suppliers: A & C American Chemical Ltd., CIL Inc., and JT Baker Chemical Company. Costs range from $230 to $4500/ton.

TABLE 18 RECOMMENDED COVERING MATERIALS FOR SPECIFIC CHEMICALS (Robinson, 1979)

Spilled Chemical	Recommended Cover
Aluminum fluoride	Inert
Calcium fluoride	Alumina
Asphalt	Inert
Barium carbonate	Inert, calcium sulphate, ferric sulphate
Calcium hydroxide	Inert, sulphate, carbonates - limestone
Lead arsenate	Inert, basic materials - limestone
Phosphorus, red or white	Sulphur, pyrite, solid oxidizing agents
Sulphur	Inert, basic materials - limestone
Organic chemicals	Inert

TABLE 19 SELECTED ACTIVE COVERING AGENTS: COST, APPLICATIONS, AND SPECIFIC GRAVITY (adapted from Hand et al., 1978)

Cover	Spilled Material	Typical* Costs ($/ton)	Specific Gravity	Comments
Iron sulphate	Calcium hydroxide	$4500	3.1	Weakly acidic; hydrous iron oxide may form under aerobic conditions- scavenging of metal.
Alum	Calcium hydroxide	$295	1.7	Weakly acidic, may form hydrogen sulphide. Hydrous aluminum oxides may form when aerobic.
Limestone	Lead arsenate	$230	2.7	Weakly basic; pozzolanic.
Sulphur	Phosphorus	$670	2.0	Considered as hazardous when spilled.
Alumina	Aluminum fluoride, Calcium fluoride	$306	4.0	Absorbs fluoride.
Potassium	Phosphorus	$4150	2.7	Strong oxidizer, could be toxic to benthos, produces hydrous manganese oxides.

* measured in tons, U.S.$ (1978)

4.3 Sealing Agents

4.3.1 Grouts and Cements. When placed on top of contaminated sediments, cements and grouts harden to form a crust, preventing the erosion and resuspension of the contaminated material. Work on dredged material stabilization and deep-mixing of contaminated sediments has been done in Japan, and grouting is commonly used in the offshore oil production industry. The technology for the use of grouts in a saltwater environment is well developed and could be easily adapted for use in capping contaminated sediments.

Sediment solidification can be achieved by three basic methods:

i) the sediment is removed, solidified and returned to the site;
ii) the area is dewatered and the sediment is solidified in-situ; or
iii) bottom sediments are solidified in-situ, using a ship or barge to deliver the solidifying material.

Although the latter is the most desirable and practical in a spill situation, there are few examples of its use. The main reasons for this are: 1) water is contaminated by agitation of sediments and solidificant; 2) the solidified strength is not increased very much since part of the surface layer of the sediment is drawn in large quantity; and 3) adverse effects surrounding benthos are of concern (Kita and Kubo, 1981). There is little experience with in-situ solidification and state-of-the-art technology for in-situ solidification is not available in North America. Takenaka Komuten Co., Ltd., of Osaka, Japan, has developed a system for the dredging, treatment, chemical fixation, and land disposal of highly contaminated harbour sediments. The sludge is mixed with a portland cement-based additive to form a chemically inert, stable soil capable of supporting heavy construction. This system is no longer being marketed in North America. Information on this system can be obtained from Takenaka Komuten Co., Ltd. (see Appendix A).

Cement-forming compounds such as portland cement, gypsum and lime are recommended, as opposed to organics such as chemical grouts, asphalts and resins which are much more expensive. In addition to the high cost, many chemical grouts contain materials that are themselves hazardous, though studies pertaining to their effect on the environment are sparse.

Studies have shown that fast-setting cement and grouts are the most resistant to erosion and dilution; however, they are not expected to hold under turbulent conditions. Permeability is generally low but will vary with the specific sealing agent, soil conditions, and application technique. The possibility of cracking as consolidation of underlying sediment occurs requires that a layer of inert material be overlaid. This will also provide additional stability and habitat for benthic organisms.

Grouting would be most useful as a barrier in low current areas and would be best used in conjunction with chemical additives that would neutralize the chemicals trapped below it. This technique would not be appropriate for liquid spills, except where the liquid has migrated completely into the sediment.

4.3.2 Polymer Films. Synthetic membranes that are resistant to hazardous chemicals can be used as a temporary containment measure for insoluble sinking materials in water. A barge-mounted application system has been proposed, though it has never been field tested (Shields and Montgomery, 1984). The major limitation is the cost of the equipment required to place the membrane.

Membranes are available in a wide range of plastics and elastomers including:

- Polyethylene (low density and high density)
- Polyvinyl chloride (PVC)
- Butyl rubber
- Ethylene propylene diene monomer (EPDM)
- 3110 (Du Pont trade name - elasticized polyolefin)
- Chlorinated polyethylene (CPE)
- Neoprene
- Chlorosulphonated polyethylene (Hypalon)
- Shelter-Rite XR5 (Seaman Corporation trade name)
- Polypropylene

Each membrane is resistant to a wide variety of hazardous chemicals; however, it is recommended that the manufacturer be consulted before using a particular membrane material with a specific hazardous substance or treatment process. If used in conjunction with neutralization, the exothermic reaction requires that the liner be able to withstand elevated temperatures.

Examples of the membranes' physical properties are given in Table 20. Membranes are available in sheet form in standard sizes up to 12-m wide, 200-m long and 1 to 5 mm thick depending on the material. The sheets can be provided with reinforcing fabrics for added strength. The panels or sheets are transported to the spill site where they are seamed together using heat sealing, cementing or solvent welding techniques.

Unterberg et al. (1984) suggested that water current and depth problems limit the use of membranes to non-navigable or shallow waters. Chemical grouts may have a detrimental effect on biota. Polymer film application systems have not been field tested

TABLE 20 PROPERTIES OF SYNTHETIC MEMBRANES (Solsberg and Parent, 1986)

Property	Polyethylene		PVC*	CPE*	Polyp-ropylene	Butyl Rubber	Hypalon	EPDM*
	low density	high density						
Specific Gravity	0.92 to 0.94	0.94 to 0.96	1.24 to 1.30	1.35 to 1.39	0.9 to 0.91	0.92 to 1.25	1.4 to 1.5	1.15 to 1.21
Tensile Strength (kPa)	8963 to 17 239	16 548 to 33 096	17 238 to 24 133	12 411	27 580 to 220 640	6895 to 27 580	6855 to 13 790	8964 to 10 343
Elongation (%)	200 to 800	10 to 650	250 to 350	375 to 575	40 to 400	300	300 to 500	300
Operating Temp. (°C)	-57 to 82	-57 to 116	-51 to 93	-40 to 93	-51 to 104	-46 to 163	-43 to 93	-59 to 149
Resistance to acids	P-G	G	G-E	G-E	G-E	G	G	G-E
Resistance to bases	G-E	G-E	G-E	G-E	G-E	G	G-E	G-E
Resistance to oxygenated solvents	P-G	P-G	G	P	P	G-E	G	G-E
Resistance to aromatic and halogenated solvents	F-G	F-G	G	P	G	P	F	P
Resistance to aliphatic solvents	F-G	F-G	G	G	G	P	G	P

P - Poor; F - Fair; G - Good; E - Excellent

*PVC - polyvinyl chloride; CPE - chlorinated polyethylene; EPDM - ethylene-propylene diene monomer

due to their cost (\$12.00 to \$24.00/m^2 depending on thickness). Manufacturers of polymer films include: Lexcan Industrial Supply Ltd., B.F. Goodrich Canada Ltd., and Schlegel Lining Technology Inc.

4.4 Placement Techniques

Placement techniques for covering material are discussed extensively by Hand et al. (1978). A brief summary of their work follows.

4.4.1 **Hopper Dredges.** Hopper dredges are most useful in unprotected waters or deep harbour and channel areas. The minimum draft restriction of 4 m may be further limited by the mode of use of the hopper dredge.

Point dumping. Point dumping to cover a spill is a straightforward application of traditional hopper dredge operations. Materials from nearby channels or other areas could be used as cover. Precise navigation of the area and draft limitations (2.1 to 2.4 m in addition to the loaded draft is required) are the main problems associated with this technique. Other problems arise from effect of the dumped material on the bottom, particularly if the material is low moisture silt and clay, or from scour if sand is used. Either may result in resuspension of the dumped material, rendering the process ineffective. Effectiveness may also be reduced as a result of poor control of the material's final location as well as unevenness of cover.

Pump-down. The drag arm of the hopper dredge can be used to discharge the covering material a few feet from the bottom. This technique reduces the scouring, mounding, and turbulence associated with point dumping. The system would apply to hopper dredges already having pump-out capability, and would require the installation of additional piping on the dredge.

A schematic of the proposed discharge is shown in Figure 18. Dashed lines represent the piping that must be added to the existing system. The preliminary cost

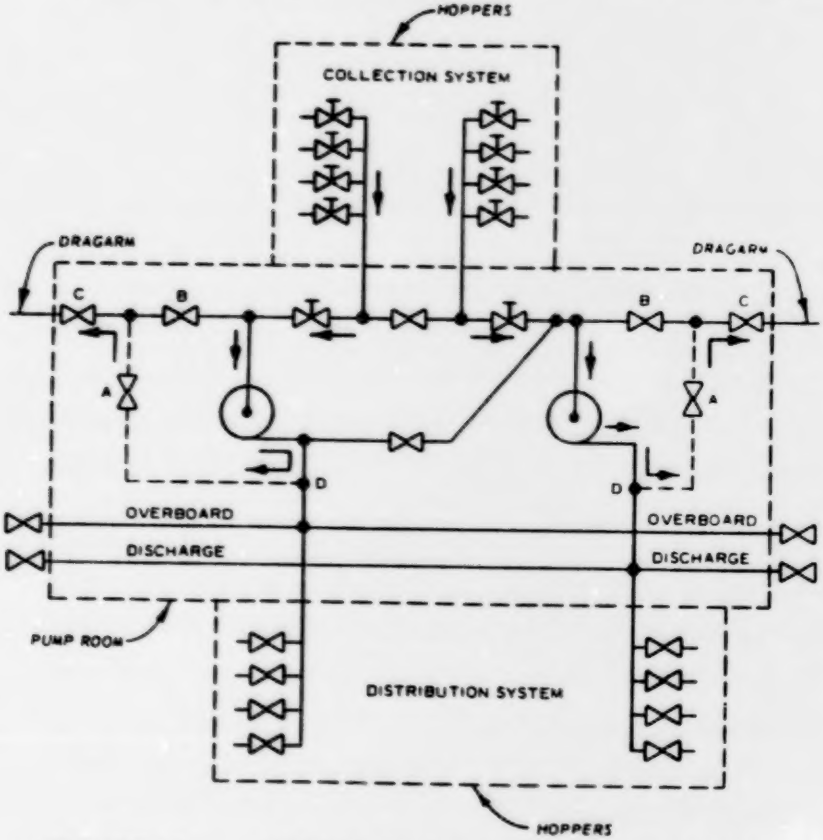


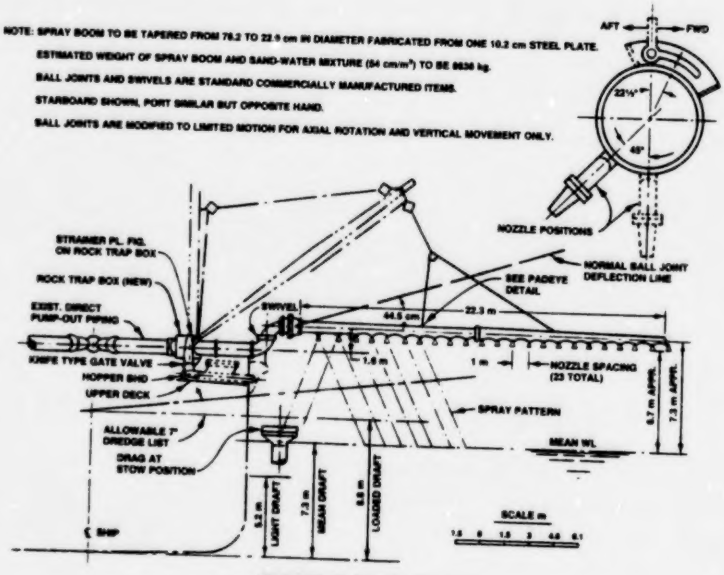
FIGURE 18 HOPPER DREDGE PIPING SCHEMATIC (Hand et al., 1978)

estimate of $150 000 (1978 U.S.$) includes engineering and design labour, installation labour and material costs.

Draft limitations are a function of the dredge. Minimum required depths would be 1.5 to 2m greater than the loaded draft, and maximum pump-down depths for effective cover vary from 15 to 20 m. Precise navigation systems should be used to increase the poor navigational accuracy that is typical of dredges.

Spray boom system. Spray booms discharge the cover material over the surface of the water where it sinks rapidly and forms a blanket over the contaminated sediment. The operation could be carried out using a hopper dredge with a direct pump-out, equipped with port and starboard spray booms and crane facilities to handle them. A proposed spray bar arrangement is shown in Figure 19. The minimum draft requirements are the same as that of pump-down configurations. Maximum depths for effective use are a function of the current and wave conditions at the time of application.

The cover material would be a slurry of approximately 10 to 20% (by weight), produced by jetting water into the hoppers and mixing at the pump inlet. Each boom is capable of laying down a swath 26 m wide. The time required for settling would depend on the depth of the water and the settling velocity of the cover material selected.


NOTE: SPRAY BOOM TO BE TAPERED FROM 76.2 TO 22.9 cm IN DIAMETER FABRICATED FROM ONE 10.2 cm STEEL PLATE.
ESTIMATED WEIGHT OF SPRAY BOOM AND SAND-WATER MIXTURE (54 cm/m³) TO BE 8636 kg.
BALL JOINTS AND SWIVELS ARE STANDARD COMMERCIALLY MANUFACTURED ITEMS.
STARBOARD SHOWN, PORT SIMILAR BUT OPPOSITE HAND.
BALL JOINTS ARE MODIFIED TO LIMITED MOTION FOR AXIAL ROTATION AND VERTICAL MOVEMENT ONLY.
AFT
FWD
22½°
45°
NOZZLE POSITIONS
STRAINER PL. FIG. ON ROCK TRAP BOX
ROCK TRAP BOX (NEW)
EXIST. DIRECT PUMP-OUT PIPING
KNIFE TYPE GATE VALVE
HOPPER BHD
UPPER DECK
NORMAL BALL JOINT DEFLECTION LINE
SEE PADEYE DETAIL
SWIVEL
44.5 cm
22.3 m
1.6 m
1 m
NOZZLE SPACING (23 TOTAL)
SPRAY PATTERN
ALLOWABLE 7° DREDGE LIST
DRAG AT STOW POSITION
MEAN WL
8.7 m APPR.
7.3 m APPR.
5.2 m LIGHT DRAFT
7.3 m MEAN DRAFT
8.8 m LOADED DRAFT
℄ SHIP
SCALE m
1.5 0 1.5 3 4.6 6.1

SECTION AT FR. 80 LKG. FWD

FIGURE 19 PROPOSED SPRAY BAR ARRANGEMENT (Hand et al., 1978)

Estimated cost of the spray boom modifications to a Geothals dredge is approximately $200 000 (1978, U.S.$). This cost does not include a precision navigation system that would be required for accurate placement of the cover. Operating costs were estimated at $3500/ha.

The primary drawback for use of this system during an emergency is the excessive time required to lay down an adequate cover. For example, it has been estimated that to cover an area 0.6 x 0.3 km with 15.24 cm of sand where the cover material to be dredged is 16 km away would take 430 hours or three calendar weeks (Hand et al., 1978). This severely limits the value of this system as an emergency response technique.

4.4.2 Hydraulic Dredge/Barge-scow. The use of barges, scows and combinations of these permits a number of placement methods. Possibilities include open-ended discharge from a hydraulic dredge, point-dumping from scows, pump-down from loaded scows and submerged pipeline discharge of dredged or other covering material. These methods will be most useful in confined areas, because unlike the hopper dredges, they are not severely restricted by draft. Depending on the size, hydraulic dredges can operate in as little as 0.6 m.

The primary disadvantage of hydraulic dredges, submerged discharge and pump-down apparatus, is their limited utility in open waters; seas as little as 0.9 m can render them temporarily ineffective. Barges and scows powered by tugboats tend to be more stable and therefore are somewhat less restricted by sea conditions. Swell-compensated cutterhead dredges claim to be operable in 1.8 m seas.

Open-pipe discharge. Open-pipe discharge is commonly used in conjunction with hydraulic dredges and would require no new hardware. This method would be used primarily in protected waters and would likely consist of direct use of dredged material for burial.

A schematic of the barge is presented in Figure 20. A floating discharge line is attached to the discharge connection of a hydraulic dredge. This arrangement allows covering in relatively shallow water while the dredge is operating as far away as 6000 m for a 75 cm dredge. Minimum working depths range from 0.9 m for a 15 cm dredge to 0.9 m or more for dredges less than 70 cm. Unless submerged pipes are used, where digging depths of 90 m are possible, the maximum depth is normally up to 20 m.

The settling characteristics of the cover material will vary, depending on the particle characteristics and cohesiveness. Coarse-grained material will settle discreetly

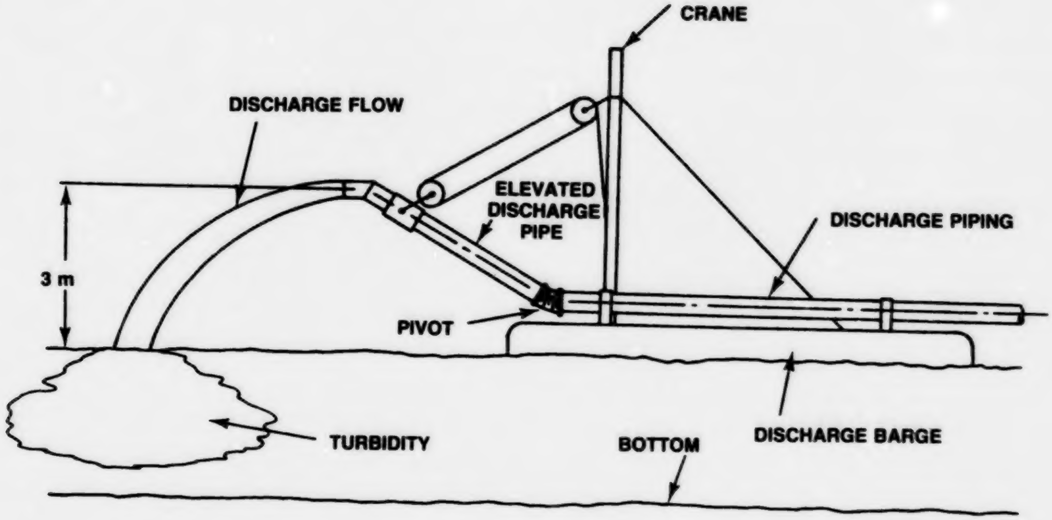


FIGURE 20 OPEN PIPE DISCHARGE BARGE (Hand et al., 1978)

whereas silts and clays will often form a mudflow and turbidity plume in the water column. Dispersion studies of sandy dredged material revealed that no subsurface sediment flow occurred, thereby requiring that the discharge end of the pipe be moved over the spill site for effective covering. The mudflows associated with fine-grained, cohesive sediments can travel radially to distances of a thousand metres or more. These mudflows can reach 0.6 m depths and travel in and out of depressions, uphill and against currents. Strong currents (unspecified in the literature) may prohibit the formation of density currents by turbulent mixing, and can sweep away the cover before it can build up into a layer.

Mudflows can be effective in covering a spill if properly controlled. The use of dykes is an effective method of confinement, since they would confine the mudflow within the specific spill area while also serving to mitigate outside currents and sources of turbulence on the spill.

Submerged discharge. Submerged discharge techniques would be used in conjunction with existing hydraulic dredges or scows and would be subject to the same environmental limitations. The use of a submerged pipe or a specially designed barge-mounted diffuser system has several improvements over the above-water, open-pipe discharge techniques: increased control over placement, reduced turbidity, and more predictable bottom flow characteristics of the discharge.

Impact velocities on the bottom can be reduced by varying the height of the discharge above the bottom and the discharge velocity. This will greatly reduce the possibility of scour and resuspension.

Complete cover can be ensured by repositioning the barge as necessary. This can be achieved with workboats and mooring tackle. The need for repositioning will be greater when sand is used because of its tendency to mound.

Three designs for spreading the cover material are found in the literature: the diffuser, a telescoping tremie tube, and a sand spreader.

Diffuser. The diffuser section uses a radial divergence of flow to slow the discharge velocity. The diffuser discharge, Figures 21 and 22, would be raised and lowered by a derrick on the barge. The difficulty in lowering and controlling the diffuser device limits it use to depths of 90 m or less, depending on the environmental conditions. Use of the diffuser would provide more control over placement of the cover, and would reduce turbidity and scouring. Phenomena similar to mudflow are not expected to occur, but "mounding" and the creation of shoal areas are more likely.

Tremie Tube. The telescoping tremie tube was used in a series of sand overlay tests in Hiroshima Bay, Japan (Figure 23). Attached to the bow of the barge, the depth can be adjusted with a discharge capacity up to 2000 m^3/h. Turbidity was virtually nonexistent with suspended solids concentrations remaining below 5 ppm. The optimum spreading method (evaluated on the bases of sand layer thickness, evenness of cover, stirring up, settling and turbidity) was the successive placement of two covering layers with the discharge 10 to 12 m above the bottom.

Sand Spreader. Using this method, sand is sucked from the barge unloader, mixed with water (to promote spreading in a thin layer), and fed through the sand spreader. The sand spreader was also tested in the sand overlay trials in Hiroshima Bay (Figures 24, 25). For the test, dyke enclosures were formed with oyster shells using a grab dredge. The sand spreader was observed to be more accurate when placed at 10 m above the bottom than when placed at 15 m. Resuspension of the bottom sediments was not observed above 1.5 m. Conspicuous irregularities in the cover were not detected.

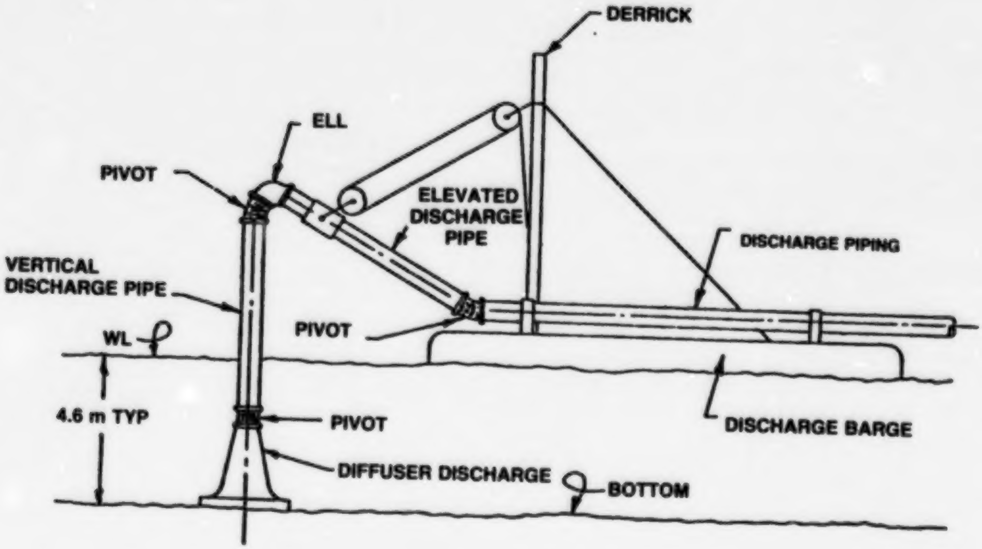


FIGURE 21 FULL-SCALE DIFFUSER CONCEPT (Hand et al., 1978)

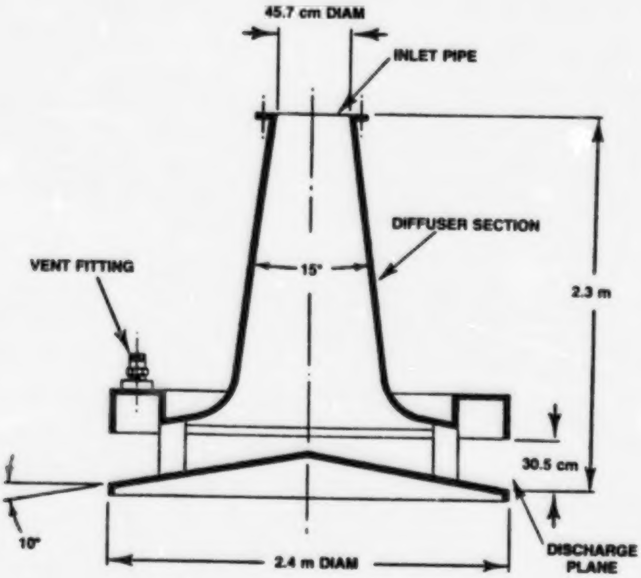


FIGURE 22 DIFFUSER (Hand et al., 1978)

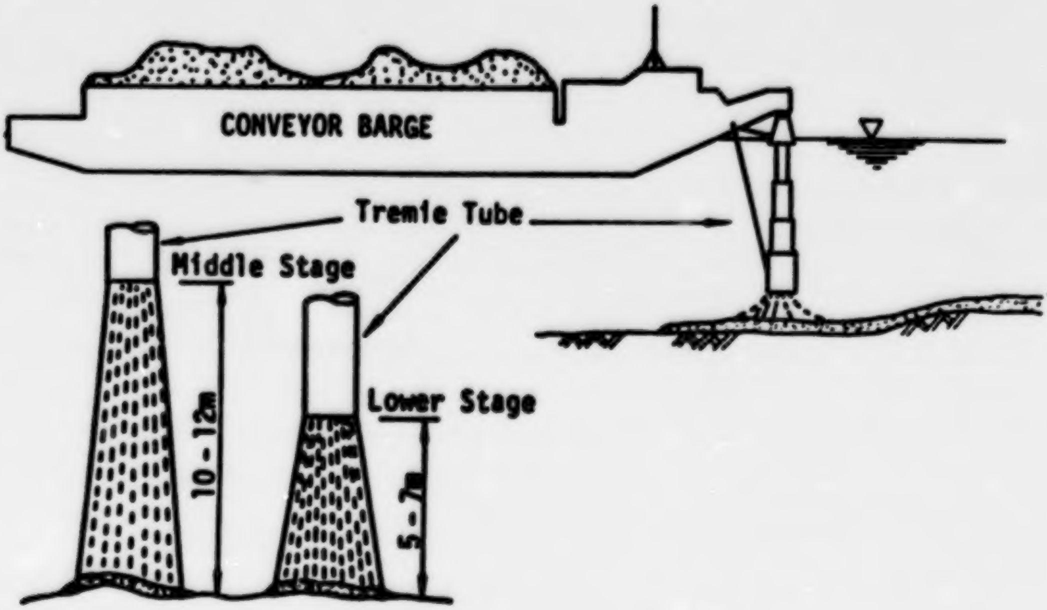


FIGURE 23 SAND DISCHARGE BY CONVEYOR BARGE (Togashi, 1981)

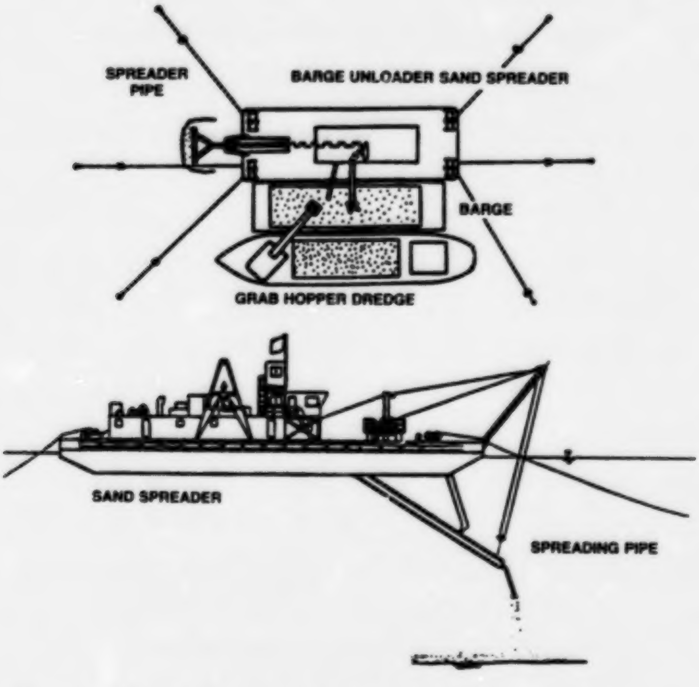


FIGURE 24 SAND OVERLAY BY BARGE UNLOADER AND SAND SPREADER (Kikegawa, 1981)

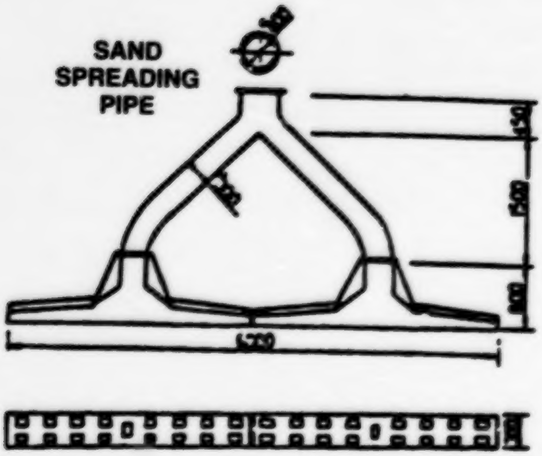


FIGURE 25 SAND SPREADER (Kikegawa, 1981)

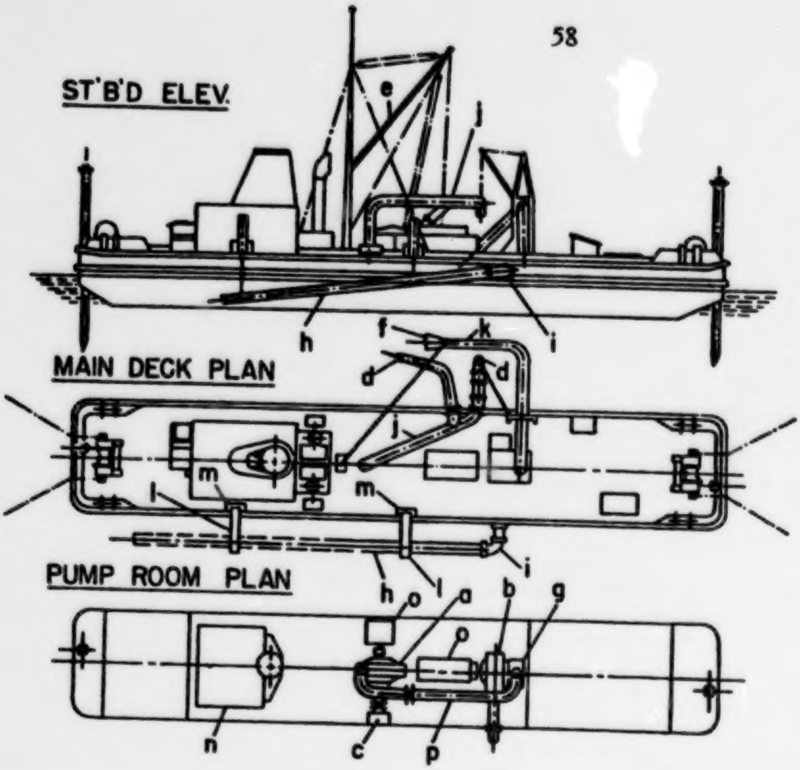
Point-dump methods (barge and scow). Point-dump methods involve the use of a hydraulic dredge in conjunction with barges and scows. The dredged material is pumped into a barge or scow which is then towed to the dump site. At the site, the material is bottom dumped.

Sizes of barges and scows range from 150 to 3000 m^3 in capacity, with drafts ranging from 2 to 6 m. Depending on barge size, door configuration, wave conditions, etc., the draft requirements restrict this method to use in waters at least 3- to 4-m deep.

The behaviour of the dumped material would be the same as for hopper dredge bottom dumping, discussed previously. Completeness of cover and impact on the bottom would again be of concern. The impact of material hitting the bottom may cause scouring and resuspension.

Pump-down methods. The unloading of a barge by pumping the material through a discharge pipe to within a metre of the bottom will reduce sediment resuspension problems. The typical features of a pump-down barge are illustrated in Figure 26.

For burial purposes, the pump-down barge would be moored in place with scows and barges tied alongside. Equipment on the unloading barge would then be swung over the hopper of the scow and the load hydraulically pumped out. The discharge pipe



a.	jet spray pump	i.	pump-down elbow, pivoting hull
b.	dredge pump	j.	jet water lines
c.	sea chest	k.	suction pipe
d	spray nozzles	l.	pump-down davits
e.	cranes	m.	pump-down winches
f.	suction head	n.	diesel power plant
g.	stone chest	o.	hydraulic motors
h.	pump-down arm	p.	priming pipe

FIGURE 26 PROPOSED PUMP-DOWN BARGE (Hand et al., 1978)

would be similar in configuration to a drag arm on a hopper dredge, or could be modified to accommodate a diffuser as in Figure 21.

Several methods of installation for the pump-out of barges are possible. The vessel could be secured with mooring lines in such a manner that it could move itself along a dump track. Alternatively, the unloading barge could be self-propelled such that it could both position itself over the spill area and tow the adjacent scow. This would permit continuous discharge while underway.

When using silts and clays for cover material, it may be necessary to provide submerged barriers to control the resultant mudflow. As sand and gravel do not flow in such a manner, dykes would not be required; however, precise positioning and movement of the unloading barge would be necessary to obtain an effective cover. Both bottom roughness and precise navigation requirements could pose problems if this technique is used.

The estimated cost for a pump-down barge 45 x 10 m is $3.5 million (1978 U.S.$); however, this could be reduced by modifying a hydraulic suction dredge. Only the cost for equipment for scow unloading would have to be added.

4.4.3 Other Placement Methods.

Mechanical dredges. There are two main types of mechanical dredges: the clamshell dredge, which is traditionally used in softer sediment, and the dipper dredge, which is generally used in harder sediment. Due to the difficulty in removing the cover material from the scow, the dipper dredge is not appropriate except when used in conjunction with a clamshell.

In conjunction with barges or scows, covering material may be placed by a series of discrete dumps using the clamshell operating in reverse. Turbulence and resuspension should not be a problem although some material will be lost into the water column during lowering unless an enclosed bucket is used. Problems of slowness and completeness of covering will exist. Operation of this type of equipment is limited to protected river and harbour areas and waters less than 30 to 40 m deep.

Barge-mounted roller apparatus systems. These systems have been suggested for hot or cold applications of polymer film overlays (Widman and Epstein, 1972). They have never been field-tested.

Three systems were considered: systems for laying down coagulable polymers, hot melt materials, and preformed, commercially available film. All three systems are similar, consisting of a barge-tug arrangement (Figures 27 and 28).

Commercially available film systems were found in theory to be easy to apply but they were expensive. A film up to 6-m wide could be deployed in "moderate" (7.6 to 9.1 m) depths over relatively flat or gently rolling terrain. The most obvious problem with such a system would be the release of gases produced in the sediments that would cause the film to bubble up, as well as weighting and puncturing problems.

Deep chemical mixing systems. Systems that mix cement and lime with fine-grained cohesive sediments for bottom stabilization have been developed in Japan. Two methods have been devised: The "Deep Cement Mixing Method" which uses portland cement, and the "Deep Lime Mixing Method" which uses quicklime. Both systems operate

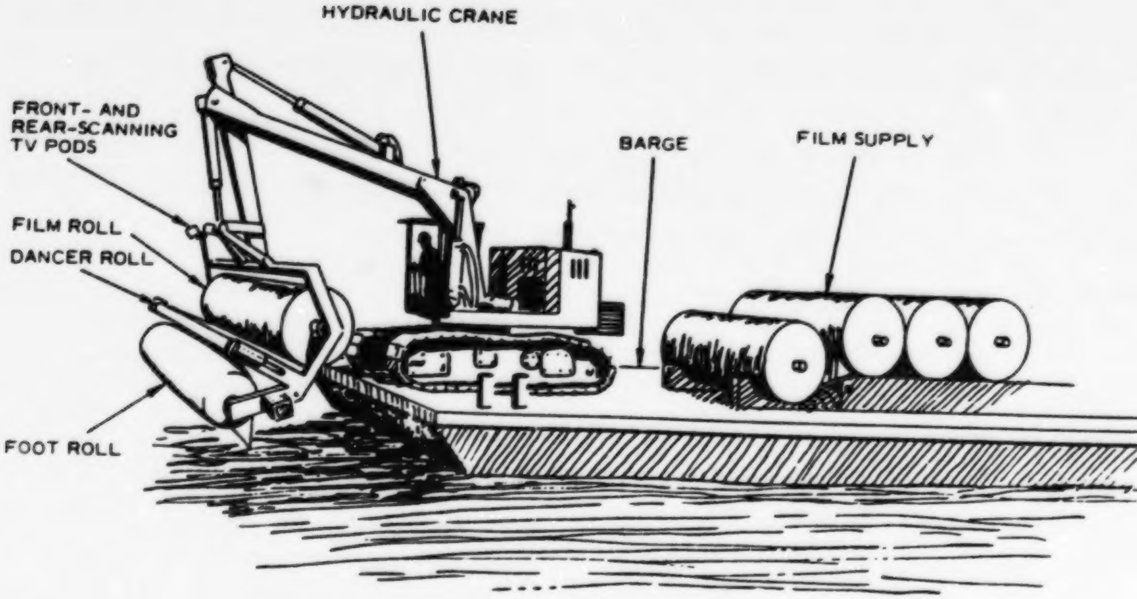


FIGURE 27 DECK ARRANGEMENT FOR BARGE-MOUNTED ROLLER APPARATUS (Hand et al., 1978)

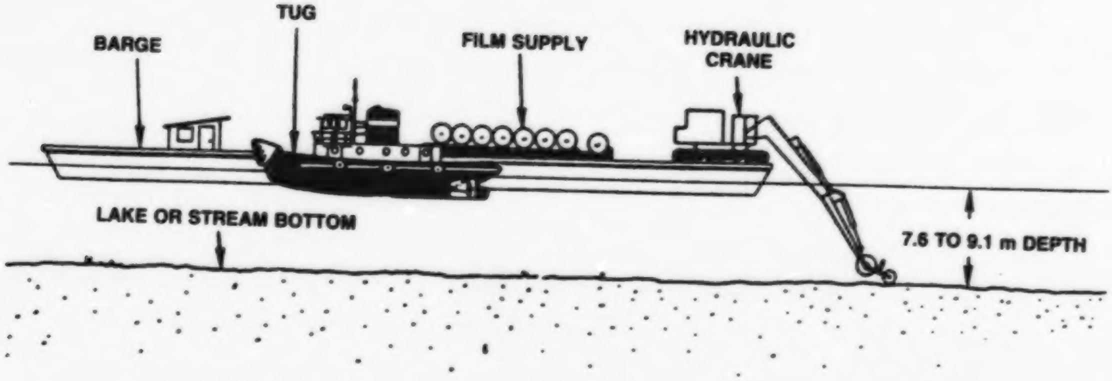


FIGURE 28 OVERALL FILM OVERLAY EQUIPMENT ARRANGEMENT (Hand et al., 1978)

by forming columns of mixed sediment that harden and increase the loading characteristics of the bottom.

The deep cement mixing apparatus is shown in Figure 29. The mixing pipes enter the sediment and the cement-based slurry is injected. Sediments are treated in pile form, creating a composite of mixed and unmixed areas. Harbour test have been done to depths of 9.1 m.

This system is limited to protected river and harbour areas during fair weather conditions. Emergency pretreatment may be required as transportation to the spill site would be slow.

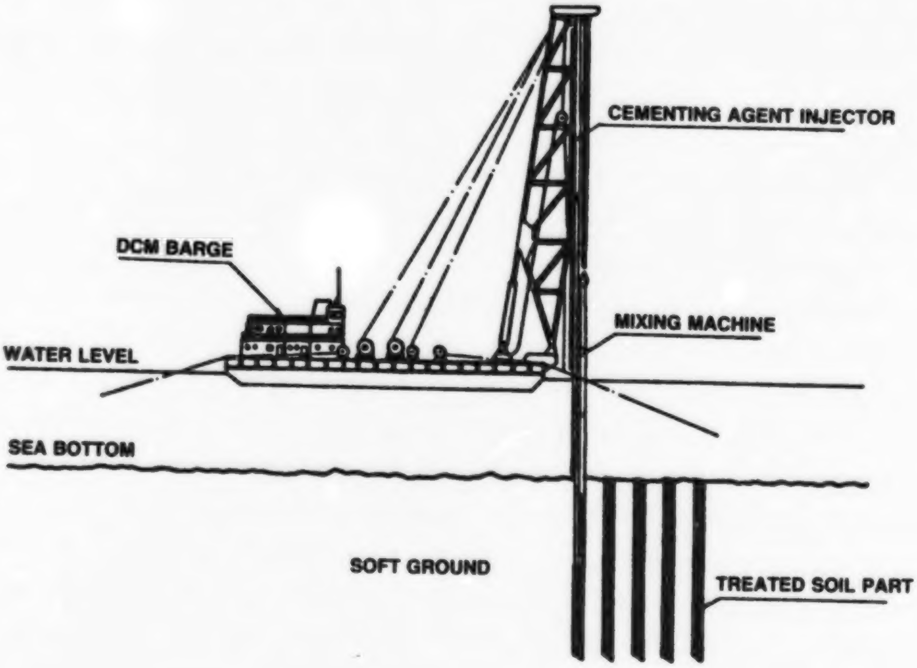


FIGURE 29 CONSTRUCTION BY DEEP CHEMICAL MIXING METHOD (Hand et al., 1978)

5 PHYSICAL TREATMENT PROCESSES

5.1 Sorption

Sorption of liquids occurs by absorption or adsorption. In absorption the liquid is mechanically entrapped within the pores and interstices of the sorbent material through capillary action. In adsorption, a weak chemical bond is formed between the liquid and the surface of the sorbent particles.

Sorption processes have long been considered as one of the most promising treatment methods for spills of hazardous materials in water. Although used extensively in the cleanup of oil spills, sorbent use for other hazardous materials has not been practised or studied to any great extent.

There are three main classifications of sorbents: natural organic, natural inorganic, and synthetic. Natural organic sorbents include natural products such as feathers, wool and cellulose. Natural inorganic sorbents include clay, diatomaceous earth and perlite. Synthetic sorbents include polyurethane, activated carbon, and polypropylene. Each category differs in terms of material origin, cost and effectiveness. Both natural and synthetics can be treated to improve their versatility and sorption capacity; treated natural sorbents are classified as synthetics.

The sorption capacity is a function of the viscosity of the spilled liquid and the characteristics of the sorbent. High fluid viscosity causes an increase in adsorption by promoting adherence between the liquid and sorbent molecules. Conversely, high viscosity inhibits absorption of the liquid into the capillaries and interstices of the sorbent. As viscosity is a function of temperature, the ambient temperature will play a role in determining what sorbent should be used.

Although natural sorbents are generally more readily available and less expensive than synthetics, the synthetic sorbents tend to have a higher sorption capacity and greater versatility. Relatively little data is available on the sorption capacity of various sorbents. Although the capacity tends to increase with price, the increase is not usually commensurate; therefore, the less expensive sorbents are often more cost effective.

Care must be taken to avoid the use of incompatible sorbents; certain sorbent-liquid combinations can result in explosion, fire or generation of toxic fumes. Data gaps limit the knowledge of compatibility between hazardous liquids and sorbent materials.

The U.S. Environmental Protection Agency compiled a comprehensive list of the compatibility and sorption capacity of selected representative liquid-sorbent pairs (Melvold et al., 1987).

5.1.1 Application to Sunken Chemicals.

There are two opinions in the literature with respect to the feasibility of using sorbents for in-situ amelioration of sunken chemicals. According to Akers et al. (1981):

> "Use of absorbents for treatment of water spills will probably be limited to those substances that are insoluble and float on the water surface...dense organic liquids that sink in the water column cannot be effectively removed by absorbents. The problem is relating the degree of organic solubility to a treatment rating for synthetic absorbents in terms of 'good', 'fair', and 'poor' removability from water."

Other authors (Hand et al., 1978; Soden and Johnson, 1978) felt that the application of sorbents for hazardous chemicals that sink held promise as an amelioration technique. It was considered that the use of sorbents would be most effective for cleanup in non-navigable waters, difficult to reach port and harbour areas, and along or in close proximity to riverbanks. Greatest efficiency would be achieved in shallow water as deployment, deployment accuracy and retrieval problems would be minimized. It should be emphasized that this response effort will not eliminate a spill but only reduce its impact.

There is no documented use of sorbents for the amelioration of chemical spills that sink in water.

5.1.2 Sorbent Types

Natural organic sorbents. Natural organic sorbents include products such as cellulose (straw, sawdust, bark, peat), feathers, and wool. Although they have been used for years in the cleanup of floating oil spills, little data is available on their sorption capacity for other organic liquids. It is known, however, that organic sorbents tend to have a greater sorption and retention capacity for organic rather than inorganic liquids.

Natural sorbents are presumed to be nontoxic although data confirming this is not available. Highly degradable organics, however, can pose somewhat of a pollution threat themselves by virtue of the high BOD that they impose on the environment. Immediate removal of the contaminated natural sorbent is necessary as their retention capacity is known to be poor.

Natural organic sorbents are limited in that their rapid desorption rate requires immediate removal of the contaminated sorbent and particulate forms have to be used with a containing shell and some weights in order for them to contact sinkers.

The primary advantage of using natural organic sorbents is their availability. They can often be obtained in isolated rural and urban areas. They can be purchased in several forms: as particulate, in pillows, or as booms.

These are the least expensive sorbents. Prices range from $0.02 to 0.04 per kg (U.S.$, 1984) (Unterberg et al., 1984). More information on costs and suppliers is provided in Appendix B.

Natural inorganic sorbents. Natural inorganic sorbents include clays, diatomaceous earth, fullers earth, perlite, vermiculite, expanded shale and natural zeolite. Clays are used solely for land spills. Mineral absorbents can be used to absorb hydrocarbons, acids and derivatives, alcohols, aldehydes, ketones, esters and nitrogen compounds.

Clays are not recommended for water spills with the exception of phenol and particulate application has to be done with a containing shell and weights in order for them to contact sinkers.

Inorganic sorbents are readily available, though usually only in particulate form.

Natural inorganics are as inexpensive as natural organics. Costs range between $0.04 and 0.08 per kg (U.S.$, 1984) (Unterberg et al., 1984).

Synthetic sorbents. Synthetic sorbents are specially manufactured to absorb organic liquids while repelling water. Synthetic sorbents have been specifically designed for organic material, and are therefore not expected to be effective in the sorption of inorganic liquids. Water soluble or miscible polar substances are rated as poorly removed by synthetic sorbents.

Synthetic materials are nontoxic and do not present a hazard when they are uncontaminated. Most synthetic sorbents can be regenerated by squeezing or wringing. This property is generally considered advantageous and cost effective; however, it could also lead to the accidental re-entry of the pollutant back into the waterbody.

Their natural buoyancy may cause some difficulties in their application to sinkers recovery. Addition of weights may be necessary.

Synthetic polymers vary in cost from \$5.00 to \$9.00 per kg (U.S.\$, 1984) (Unterberg et al., 1984). The sorption capacity tends to increase with cost, but not commensurately.

Macroreticular resins. Macroreticular resins are polymers with a spongy or reticulated structure produced by cross-linking of linear polymers. These resins can exhibit absorption characteristics as well as adsorption and ion exchange characteristics.

Macroreticular resins sorb liquids. solutes and dissolved solids. They are known to sorb phenol and aldrin and are considered to be more versatile than polyurethane foam, but less so than activated carbon. The literature cites no examples of their use in a spill cleanup and practically no research has been conducted on large-scale use.

Resin regeneration capabilities have not been ascertained. Due to their thermal sensitivity to bond cleavage and oxidation, desorption by heating is not possible. Eluent, airstream, and vacuum desorption with recovery of sorbate for disposal are considered to be viable regeneration alternatives (Unterberg et al., 1984). At present, regeneration is not possible in the field.

Due to the present low level of use, availability on short notice is likely to be a problem. Little research has been conducted on their use for spill cleanup, and regeneration capabilities are unascertained.

Macroreticular resins are not readily available though they can be purchased through Rohm and Haas Co., Philadelphia, PA. They can be purchased in particulate form or as sorbent pillows.

Polyurethane. Polyurethane polymer is produced in open pore, closed pore, and nonporous particulate form. Although capable of sorbing a variety of chemicals, polyurethane is not as versatile as activated carbon. The sorption capacity, ranging from 0.1 to 80 times their own weight, is a function of the open-volume porosity and the viscosity and wetting power of the spilled hazardous chemical.

Polyurethane foams have reportedly been formed on-site which could prove advantageous. Their use is not considered to contaminate water, though it may pose a fire threat to handlers. Studies revealed that Sorbent Science Corp's "Absorbent" is nontoxic to brine fish and California killifish at concentrations ranging from 0.5 to 10.0 g/mL (Akers et al., 1981). No biodegradation or chemical degradation in seawater was observed.

Polyurethane can be formed and regenerated on-site to avoid bulk transport problems. It is generally available in larger metropolitan areas and can be purchased as foam, in mats, belts, pillows and sheets. Suppliers include: the BASF Wyandotte Corp., the Industrial Chemicals Group, and the B.F. Goodrich Chemical Company.

Polypropylene. Polypropylene is a linear hydrocarbon polymer. It is inherently oleophilic and therefore absorbs covalent liquids or solutes. It cannot be exposed to high-solvency liquids and is less versatile than polyurethanes. Even though it is less versatile than macroreticular resins, it is considered more feasible for present-day use because it can be applied and collected with existing devices.

Polypropylene is not considered to contaminate water. 3M's "Oil Absorbent," a product made from polypropylene has U.S. Food and Drug Administration (FDA) approval and is therefore considered nontoxic to humans. Tests on fish have not been done.

Regeneration for reuse with polypropylene sorbents is possible. Mop wringers and squeeze roller systems have 50 to 75% removal with 10 to 20 cycles possible. The 3M Company has undertaken tests to evaluate the removal efficiency of centrifugation. Tests have shown 90% oil removal with very high total sorption capacity retained.

Polypropylene can be purchased as belts, mats, pillows or sheets. Polypropylenes of higher average molecular weight, isotacticity and crystallinity have better solvent and chemical resistance. Improved resistance widens their applicability but increases their fabrication costs. Lower cost byproduct poly, recycled poly and waste poly can also be utilized.

Polypropylene is available from 3M Canada Inc. and Sorbent Products Co., Inc.

Activated carbon. Activated carbon (AC) in various forms has been proposed for adsorbing spilled, water-soluble hazardous chemicals from waterways.

Activated carbon adsorption can remove organics and some inorganic chemicals from water. Because of its availability, applicability, and versatility it is considered to be the most valuable chemical agent for present-day use in the amelioration of hazardous chemicals spills in water. Bauer et al. (1976) suggest that activated carbon may be useful in adsorbing virtually all sinking chemicals, the exceptions being the sinking solids: barium carbonate, lead arsenate, phosphorus, triethanolamine and liquid mercury. Information on the amenability of various organic sinkers to AC adsorption is presented in Table 21. Compounds not adsorbed by AC are listed in Table 22.

Different activated carbons are selective for different hazardous chemicals. The carbon surface, ranging from 500 to 1000 m^2/g, can be acidic or basic, hydrophilic or hydrophobic, oleophilic or oleophobic. The effective density, determined by the particle porosity and interparticle packing, can range from 0.09 to 2.0 relative to water.

TABLE 21 AMENABILITY OF SINKING ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION (adapted from Akers et al., 1981)

Compound	Sorption (g compound/g carbon)	% Reduction of Initial Concentration
Acetic acid	0.048	24
Acrylic acid	0.129	64.5
Aniline	0.15	74.9
Benzaldehyde	0.188	94.0
Benzoic acid	0.183	91.1
Diethylene glycol	0.053	26.2
Dipropylene glycol	0.033	16.6
Ethylene dichloride	0.163	81.1
Ethylene glycol	0.0136	6.8
Formaldehyde	0.018	9.2
Formic acid	0.047	23.5
Hydroquinone	0.167	83.3
Phenol	0.161	80.6
Tetraethylene glycol	0.116	58.1
Triethylene glycol	0.105	52.3

Note: Initial Concentration = 1000 mg/L

TABLE 22 EXAMPLES OF SINKERS NOT ADSORBED BY ACTIVATED CARBON

Barium carbonate
Lead arsenate
Liquid mercury
Phosphorus
Triethanolamine

Activated carbon with a specific gravity greater than one could be particularly effective for in-situ adsorption of sunken chemicals. Activated carbon is available in several forms including powdered, granular, rod, sheet and others.

The mechanisms for carbon adsorption are not understood, but empirical observations of adsorption phenomena allow generalizations of the process.

The adsorptive capacity of the AC for an organic pollutant is a function of the characteristics of the AC being used, the material being adsorbed and the solution the material is in. Important factors include the solubility of the contaminant, its molecular size, polarity, specific gravity and structure as well as the type of AC being used, the temperature and pH of the solution and the carbon contact time. The adsorption rate increases with increasing temperature, increasing molecular weight and decreasing solubility and polarity. Molecular structure has a definite influence on adsorption: hydroxyl, sulphonic and amino groups reduce adsorption because of increased polarity; aromatic and substituted aromatic compounds are generally more adsorbable than aliphatic compounds; and amines, ethers and halogenated aliphatic compounds adsorb more efficiently than low molecular weight alcohols, glycols, or low molecular weight straight chain unsubstituted aliphatic compounds (U.S. Army, 1980). Ten parts of activated carbon to one part of spilled material is generally considered near to optimum for the treatment of most organic spills.

Inorganic compounds exhibit a wide range of adsorbability. Iodine, gold permanganate, dichromate, mercuric salts, arsenates and silver salts are adsorbed; strongly dissociated salts such as sodium chloride are not. Some metal salts are chemically reduced to elemental metal by AC. Of various metals tested, mercury salts showed the highest affinity for AC. A carbon to mercury dose of 5:1 by weight effected greater than 99% removal (Ziegler and Lafornara, 1972). The amount of AC required to adsorb a specific chemical must be established by testing.

Activated carbon is available in granular (GAC) and powdered (PAC) form. Granular activated carbon is widely available and is the predominant form of AC in industrial waste treatment. Although it adsorbs pollutants less rapidly than PAC, its greater size permits greater flexibility in the design of dispersal and retrieval techniques. One particularly useful form for in-situ water spill cleanup is the carbon-filled porous cloth "teabag". It is also used in fixed beds or columns.

Powdered activated carbon is less expensive and may have a slightly higher adsorption capacity than GAC but its use for hazardous substances spills in water is limited. PAC suffers from three main drawbacks: it is difficult to regenerate without high losses; the settling characteristics may be poor making it difficult to handle; and coagulation may occur in the presence of suspended solids. Free powdered carbon is not suitable for use in natural waters except as a last resort or in situations where the contaminated powder would settle to the bottom where it could be located and removed.

Activated carbon has been evaluated for toxicity. Apart from it being aesthetically unappealing in a waterway, it is nontoxic to the human environment and is nontoxic to fish except when used in massive quantities (at high turbidity levels, AC physically interferes with the respiratory function of the gills). There is inadequate data on toxicity to benthic organisms. In general, a single application of irretrievable AC at the incorrect location is not likely to present a serious ecological effect other than the temporary aesthetic problem. Unacceptable turbidity levels have been reported with AC concentrations of 1000 ppm, and concentrations of only 1% of this value were also found to be unacceptable. With the exception of phenylurea and acid herbicides, organic material does not readily desorb; however, the persistence and therefore chronic toxicity of contaminated AC in the watercourse is not known.

When the adsorption capacity of the carbon has been exhausted, the spent carbon must be replaced, disposed of and/or regenerated for reuse. Thermal regeneration is most commonly used and can be done in the field with mobile systems. On-site thermal reactivation is only economical when carbon usage is greater than 450 kg/day (Unterberg et al., 1984). Below this point it is more economical to purchase new AC or to use a centralized regeneration facility.

Factors for *in-situ* spill treatment effectiveness applicable to all treatment concepts are:

- the time to respond,
- the water current,
- the amount of turbulence, and
- the volume of water affected.

Laboratory studies with activated carbon have shown that the most efficient adsorption is obtained with powdered activated carbon (PAC) in water that is sufficiently turbulent to keep the powder in suspension. However, concentrations as low as 1000 ppm were found to produce unacceptable turbidity levels. The addition of flocculants to decrease turbidity levels is not fully effective, and bioassays have revealed that the resultant sludge is toxic to fish. Removal by dredging is therefore necessary.

Froth flotation techniques to float the carbon particles for subsequent removal was found to be even less effective than flocculation. With the addition of surface active agents only 50% recovery was achieved. These agents may pose secondary pollution problems, sometimes equal to or greater than the first.

For obvious reasons, free-powdered activated carbon is not suitable for use in natural water except as a last resort or where the contaminated carbon would settle and be located and removed.

Several studies have been conducted to determine the feasibility of hazardous chemical removal through the subsurface injection of buoyant activated carbon (Ziegler and Lafornara, 1972; Dawson et al., 1977). The carbon is captured in quiescent waters downstream by a boom and pumped as a slurry to a storage tank. Dawson et al. (1977) determined that a recovery efficiency of 50% was possible for dissolved hazardous chemicals, with a carbon contaminant ratio of 10:1.

Beaker tests have indicated that a carbon fibre, resembling loosely-packed, fine-grain steel wool shows excellent potential for the removal of pollutants in water. The carbon fibres were determined to be as effective as powdered carbon in the removal capacity and the rate of removal. The literature contains no evidence that the material has been tested in the field.

The strength and flexibility of the fibres permits their compression for storage and shipment. When placed in water, the matrix expands and floats with the uppermost fibres at the water surface. The density of the material is very close to that of water, making it ideal for soluble chemicals. It is conceivable that slight alterations could produce a fibre that would sink to adsorb bottom chemicals. The fibre could be removed using a coarse net or a grappling hook.

This material has many of the properties of AC that make it desirable for field use. Further experimentation and development is required.

To eliminate turbidity problems and facilitate removal, AC has been packaged in porous bags ("teabags"). The bag is of sufficient mesh size to permit waterflow through the bag while containing the carbon particles. Removal efficiency is highly dependent on turbulence, wind strength and direction, and contact time.

It has been suggested that the cleanup of sinking hazardous chemicals is possible by filling the bags with AC having a specific gravity greater than 1.0 or weighting them to promote sinking. This technique has not been studied.

Limitations for using AC are: a carbon/contaminant ratio of 10:1 requires excessive amounts of AC for large spills; the in-situ use of free-powdered carbon results in unacceptable turbidity levels; technical and economic feasibility of carbon teabags is uncertain; 24 hours is required to wet the AC prior to use (wetting increases the efficiency of adsorption); a source of clean water must be available on site prior to start-up; and use of a carbon column as a filter results in inefficient use of its adsorption capabilities; clarification is usually a necessary pretreatment step prior to carbon adsorption.

Due to its widespread use, AC should be available within a day from Calgon Canada AC Division and Van Waters & Rogers Ltd. Costs for activated carbon range from \$1.10 to \$11.00/kg (U.S.\$, 1984) (Unterberg et al., 1984).

Ion exchange resins. Ion exchange resins consist of insoluble high molecular weight organic polymers containing charged functional groups that are capable of exchanging with positive or negative ions in aqueous solution. The toxic ions in a wastewater are replaced with relatively harmless ions. The ions are held by electrostatic forces to the functional groups on the surface of the ion exchange material. Ion exchange is effective in removing fertilizers, dyestuffs, pesticides, chlorine, colour and organics. The inherent low solubilities of hazardous chemicals that sink could preclude their use in many cases, and adsorption efficiency is known to be reduced in saltwater environments. For these reasons, ion exchange is generally considered to be inferior in application to activated carbon.

A wide variety of ion exchange resins are available, each one being applicable to only a small range of hazardous chemicals. The capacities of the resins can vary greatly with the manufacturer.

Ion exchange resins are used routinely in the food and water purification industries. The U.S. FDA regulations list 16 resin matrices that are approved for use in food and pharmaceutical preparation. It is not expected that their use for spill treatment would pose any hazard to the water for human consumption. Available evidence suggests that uncontaminated ion exchange resins would not produce toxicity problems if left in the environment; however, information verifying nontoxicity to fish and other aquatic life is not available.

The desorption rate of hazardous materials from ion exchangers is not known; therefore, the persistence of toxic effects cannot be addressed. Most ion exchangers are capable of regeneration with solutions of caustic or strong acid, making it unlikely to occur naturally in the environment. Because of their thermal sensitivity, desorption by heat is not possible. For unspecified reasons, Unterberg et al. (1984) claim that unless absolutely necessary, resins should not be regenerated in the field.

Ion exchange is generally considered as an external treatment process though some in-situ studies have been done with resin teabags and fully dispersed resins (Hand et al., 1978). In-situ delivery can be accomplished in a similar manner to that of activated carbon. Confinement of the resin in readily recoverable booms, pillows, and mats would allow easy retrieval, and these packages could be weighted for the recovery of bottom chemicals. Ion exchange resins rendered buoyant by incorporating hollow glass microspheres are claimed to be effective for the removal of hazardous chemicals dissolved in the water (Srinivasan, 1975).

When ion exchange is used as an external treatment process, prefiltration is necessary as suspended solids will substantially reduce the treatment efficiency. The effluent should be continuously monitored to prevent breakthrough. Trailer-mounted units have been used on a pilot-plant scale. Desirable features that make this approach promising for hazardous material spill response include the design potential for compact modular units, quick startup and shutdown, ease of operation with minimal training, and ease of automation. It is not an energy intensive process and the power required for pumping can be supplied by an on-board generator.

It should be noted that strong oxidizing agents can degrade the resins under certain conditions and cause an explosive reaction. The low solubilities of sinkers could preclude the use of ion exchange resins use in many cases. The adsorption efficiency is reduced in saltwater environments. Resins should not be regenerated in the field or used for the treatment of strong oxidizing agents.

Due to their wide range of use in the water purification and treatment industry, ion-exchange resins are available off-the-shelf from many manufacturers. Resins generally sell between $1000 and $3500/m^3 (U.S.$, 1984) (Unterberg et al., 1984).

A summary of the available information on the sorbent capacity and sorbent-liquid compatability is presented in Table 23. Only information for hazardous chemicals that sink or precipitate is presented.

Specific information on sorbents that are compatible with hazardous chemicals that sink and can be applied to water can be found in Appendix B. Hazorb (Diamond Shamrock Corporation) is compatible with a number of hazardous chemicals; however, its affinity for water renders it useless for application to spills in water, and is therefore not discussed in this report.

5.1.3 **Deployment Techniques.** Sorption may be accomplished by either column or batch treatment. Column treatment involves percolating the contaminated solution through a fixed bed of sorbent media. The media is regenerated once the sorption capacity is reached, and the cycle is repeated. Batch treatment is achieved by mixing the

TABLE 23 COMPATIBILITY OF HAZARDOUS LIQUIDS AND SELECTED SORBENT MATERIALS (Solsberg and Parent, 1986)

	Sorbent Materials									
Hazardous Liquids	Animal Materials	Activated Carbon	Cellulose (Conwed)	Calcium Carbonate	Other Minerals	Treated Minerals (Hazorb)	Polyolefins	Polypropylene (3M Absorbent)	Cross-linked Copolymer	Polyurethanes (SSC Absorbent)
Acids and Derivatives										
Acetic Acid		•	•		•			•		
Acetic Anhydride		•	•		•	•(13)		•		•
2-2 Dichloropropionic Acid			•							
Formic Acid		•	•		•			•		
Napthenic Acid		•	•		•					
Phenols										
Cresol		•	•		•	•(13)	•	•	•	•
Phenol		•	•		•	•(15)	•			•
Aldehydes and Ketones										
Formaldehyde		•	x		•	•(10)		•		•
Furfural		•	•		•			•		
Esters										
n-Butyl Phthalate		•			•			•		
Pyrethins								•		
Halogens										
Acetyl bromide		•	•					•		
Acetyl chloride		•	•					•		
Benzoyl chloride		•		•			•	•		•
Benzyl chloride		•		•				•	•	
Carbon tetrachloride		•			•	•(10)		•	•	•
Chlordane		•						•		
Chlorobenzene		•	•		•	•(12)		•	•	
Chloroform		•	•		•	•(12)	•	•(18)	•	•
Cyanogen chloride		•	•				•			•
o-dichlorobenzene		•			•			•	•	
Dichloropropane-Dichloropropene		•						•	•	
Hexachlorocyclopentadiene								•	•	
Phosgene		•								
PCBs		•			•	•(10)	•	•		•
Trichloroethylene		•			•	•(13)		•	•	
Vinylidene chloride		•						•		
Nitrogen Compounds										
Aniline		•	•							
Benzonitrile		•	•							•
Dinitrotoluene		•								
Hydrogen cyanide		•		•	•					
Nitrobenzene		•	•		•			•		
Quinoline		•	•					•		
Organometal										
Tetraethyllead		•	•		•			•		
Organophosphorous Compounds										
Diazinon		•			•			•		
Dichlorovos		•			•			•		
Disulfoton		•			•			•		
Ethion		•			•			•		
Malathion		•	•		•			•		
Methyl parathion		•			•					
Naled		•			•			•		
Parathion		•			•			•		
Sulphur Compounds										
Carbon disulphide		•	•		•			•		•
Chlorosulphonic acid		•			•	•(18)		•		
Acids										
Hydrochloric acid	x	•	x	•	•	•(14)		•		•
Hydrofluoric acid	x	•	x	•	•					
Nitric acid	x	•	x	•	•	•(20)		•		•
Phosphoric acid	x	•	x	•	•	•(26)		•		•
Inorganic Halides										
Phosphorus oxychloride		•		•				•		
Phosphorus trichloride		•		•				•		
Sulphur monochloride		•						•		
Zinc chloride (solution)		•								

•	Compatible combinations
x	Incompatible combinations
( )	Sorption capacity (mass of material sorbed per unit mass sorbent)

sorbent with the contaminated solution for a specified period of time. The sorbent is then removed for disposal or regeneration and reuse.

Column treatment is more efficient than batch treatment and greater contaminant removal can be obtained. The major drawbacks of this method are the requirement for removing large volumes of water for treatment, and the time period required to set up the necessary equipment. Batch treatment is most feasible for field use as a more rapid response and treatment minimizes the dispersal of the hazardous materials from the spill site.

The few sorbents that are denser than water include some forms of activated carbon, untreated cellulose, and untreated minerals such as sand or clay. Shuckrow et al. (1972) have suggested the injection of an activated carbon slurry below the water surface as a possible deployment technique. Mechanical injection methods would allow the sinking sorbent to be used on small and medium spills and in deeper and more open waters of ports and harbours. Sorbent slurries and injection units could be mounted on workboats for quick transport to the spill site. Containment techniques such as dyking and trenching may be required to prevent lateral dispersion due to currents. Removal of the contaminated sorbent slurry could be achieved with a handheld vacuum pump or a dredge.

The use of floating sorbents on the bottom is impossible unless special delivery systems are designed. It has been suggested that floating sorbent, in the form of booms, pads and pillows should be appropriate if weighting devices are utilized (Hand et al., 1978; Soden and Johnson, 1978). Retrieval could be aided by attaching floating markers to the sorbent. Sunken booms would have the added advantage of containing the spill if properly positioned. Mixing sorbents with inert covering material has also been suggested (Soden and Johnson, 1978). This could be accomplished by injection into the discharge line of a hydraulic dredge. There is no indication in the literature that attempts have been made to test these concepts.

Coated cotton meshwork has been suggested as a possible device for the removal of organic mercury from contaminated water and sediments. Such a technique would have potential in sorbent application to sinking chemicals for small and medium spills (Robinson, 1979). The spent sorbent could be incinerated after removal from the spill site. Evaluation of the potential of the various sorbents and coating materials must be undertaken.

Another potential technique for sorbent use is the tilling of magnetized activated carbon into the contaminated sediments and subsequent removal. This technique was developed with EPA support for use on Kepone amelioration in the James River, Virginia (Hand et al., 1978).

Brief descriptions of deployment techniques that have been studied on an experimental basis follow. Most were designed for the amelioration of dissolved chemicals; however, they could also be appropriate for insoluble sinkers as well.

Free-flowing buoyant sorbent. As stated earlier, the use of buoyant sorbent particles has been proposed for the removal of dissolved chemicals. It also offers some potential, however, for the removal of sinkers. For dissolved chemicals, the buoyant media is deposited at the bottom of the water column so that it removes contaminants as it rises to the surface.

Studies by Dawson et al. (1977) determined that buoyant carbon was superior to porous bags in terms of removal efficiency of dissolved chemicals under the spill and flow conditions tested. Floating carbon was capable of achieving 50% removal at a carbon/contaminant ratio of 10:1.

Two general application methods have been suggested:

1) Pumping bulk media as a slurry through a pipe that terminates near the bottom of the watercourse. The vessel that holds the pumping unit is propelled at a speed proportional to the application rate.
2) Dropping packages of media weighted with ballast on the surface of the water. The package material disintegrates or opens upon exposure to water after sufficient time to allow the package to reach the bottom.

Mechanical subsurface injection is considered to be the most desirable delivery method in port and harbour areas where the required equipment is readily available. However, air deployment is considered to be more feasible in remote locations where the rapid transport of subsurface injection equipment may not be possible.

Media packaging concepts for air deployment include methods that employ both retrievable and irretrievable containers. Mercer et al. (1973) evaluated the following packaging techniques: plastic containers, soluble synthetic films, unfired clay containers, and ice cakes.

Retrieval of the spent media can be achieved manually or mechanically. In flowing waters the sorbent can be intercepted downstream by positioning booms at an angle across the flow path. This will direct the media to an accessible shore area where pickup can be achieved either manually or with earth-moving equipment. Dawson et al. (1977) achieved a carbon recovery in excess of 90% with this method.

In static waters the media must be collected and removed from the water surface. Much of the technology developed for oil spill countermeasures would be applicable to the recovery of spent sorption media.

The application of free-flowing buoyant media carbon, however, is not recommended because of turbidity problems. Retrieval of free-flowing media is more complex than that of packaged media.

Buoyant media is more adversely affected by adverse weather conditions than packaged media. Recovery using booms is limited to oil booms in conditions with current.

Teabag. Porous cloth "teabags" have been suggested as a packaging technique for particulate sorbents to permit greater flexibility in dispersal and retrieval techniques.

The sorbent is packaged in a water permeable bag which allows the pollutant-laden water to pass through the bag material and interact with the sorbent. The finer the particles of sorbent used, the greater the ease of fluidization and surface contact, and the more rapid the sorption. Fine particles, however, require fine material to contain them which restricts water flow. The porosity of the bag must be consistent with the free interchange of water and the retention of the sorbent. Studies undertaken by the EPA on the use of activated carbon teabags determined that 12 x 40 mesh Filtrasorb carbon (produced by Calgon Corporation) was compatible with a polyester monofilament screen cloth with an ASTM mesh count of 51 (Kressilk Product, Inc.) (Dawson et al., 1977). Laboratory tests undertaken with ion-exchange teabags for the removal of heavy metals incorporated a mixture of cationic and anionic resins (Corning No. 3508A) with a dacron polyester fabric having a mesh size of 0.4 x 0.5 mm (Pilié et al., 1975).

Mercer et al. (1978) undertook experiments to determine the optimum teabag configuration. Tests were performed with two bag configurations:

i) 2.5-cm wide vertical pockets fully packed with carbon, and
ii) 2.5-cm wide horizontal packets half-filled with carbon.

The loose packing permitted less restricted flow of water, and the horizontal configuration prevented sorbent packing by gravity. Therefore the second bag configuration was deemed superior. As a large surface area to volume ratio permits greater adsorption, the packet should be thin.

Several techniques for the use of carbon teabags have been suggested:

1) **Weighted:** carbon teabags could be weighted to permit application to a sunken pool of liquid on the bottom of the waterway. This technique is considered to hold promise although no studies have been undertaken to determine its feasibility.

2) **Suspended:** teabags are suspended from floats, allowing them to travel at desired depths in the water. The bags travel freely in the water along with the spill plume, permitting long contact times. Retrieval can be achieved by booms or a strung wire perpendicular to the flow and just below the surface of the stream. A final degree of treatment is provided as the snared bags are analogous to a fixed carbon bed that the contaminated water flows through. Experimental studies by Dawson et al. (1977) obtained 20% removal efficiencies at stream flowrates of 0.425 m^3/s with carbon:contaminant ratios of 10:1. It was concluded that removal rates may improve with longer contact times.

3) **Cycled:** teabags are filled with a buoyant sorbent and injected at the bottom of a polluted volume of water by a solids handling pump. The packet rises through the water column and upon reaching the surface, the packets are automatically pumped down to the bottom of the water column again to start another cycle. Mathematical modelling performed by Rockwell International (1981) on this method determined that the recycling demands on the pump would be prohibitive (Schneider, 1981; Dawson et al., 1977).

4) **Panels:** panels packed with a sorbent are hung in some homogeneous pattern downstream of the spill and turned perpendicular to the flow. Because contact times are too short to achieve sufficient adsorption, this technique would only be effective if the spill was massive in comparison to the total flow of the waterway or the panel was in place very shortly after the spill (Schneider, 1981). Increasing the sorbent depth would increase the contact time; however, the increased resistance to flow would create large tension in the supporting cables and on the bags themselves.

As stated earlier, teabag flow-through is a vital factor in the removal efficiency of this technique. It is uncertain whether this technique would be effective in treating spills that occur in still-water or slow-moving streams. Investigations have indicated that the removal efficiency is directly proportional to the turbulence and current structure in the receiving water. As the flow and turbulence increases, the pollutant removal efficiency of the teabag approach improves. Still-water tests in a pool experiment showed that significant increases in adsorption rates resulted from the artificial generation of 2-cm high waves. Similar results were obtained with small artificial waves in a channel under conditions of no flow. In flowing streams and lakes, the natural turbulence and wave action should be sufficient to continually exchange the waters in the immediate vicinity of the bag. Under calm water conditions, the waves produced by a few outboard motor boats could provide sufficient agitation to enhance adsorption kinetics.

Filter fences. Melvold and McCarthy (1984) recommend the use of filter fences for the cleanup of small spills (40 to 2000 L) of insoluble sinkers in water. Filter fences have been used extensively in the cleanup of floating oil spills though no documentation of their use for sinkers has been found.

A filter fence consists of two fences of "chicken wire" about a foot apart either perpendicular or at an angle of 45° to the current axis. The space between the fences is filled with a loose sorbent. The water flow carries the spilled material into the sorbent, which will then sorb the liquid while allowing the water to flow through. The sorbent is removed and replaced when saturation occurs. This system is simple, can be constructed from a wide variety of material available in the field, is effective and inexpensive, and has been used for at least 15 years.

It is claimed that the system will work just as effectively for pollutants moving along the bottom as for those that float. It is difficult to determine when the sorbent reaches saturation, however, as the contaminants on the bottom are difficult to see. This method is only suitable for small spills; wind and currents limit its applicability.

5.2 Gelling Agents

The purpose of a gelling agent is to immobilize a spill to prevent further spread into the environment and condition the spill for mechanical removal. Gels have been used on land and surface water spills and their use has been proposed for spills of hazardous chemicals that sink (Hand et al., 1978). Several sources, however, state that gelling agents should not be used on water spills of materials that sink or mix into the water column (Unterberg et al., 1984; Akers et al., 1981). More research is required to determine the effectiveness and behaviour of blended gelling agents in water before recommendations can be made relative to their application to water spills. No literature has been uncovered to indicate that any work has been undertaken with gelling agents under water.

Baier et al. (1976) have developed a "Multipurpose Gelling Agent" that is effective against a broad range of substances as compared with other gelling agents. With some modifications, it is suggested that this material could be used for the immobilization of hazardous chemicals that sink.

5.2.1 Application to Sunken Chemicals. The feasibility of in-situ application of gelling agents to sinking chemicals is largely unknown although a number of chemicals that sink have been shown to be immobilized by the Multipurpose Gelling Agent (Table 24). It may be possible to gel a sinker in-situ by bringing the gelling agent into close contact with the spilled liquid. A pressurized delivery system with a broad dispersion head could be used. The major difficulty is the tendency of the gelling agent to

TABLE 24 SINKERS TESTED WITH THE MULTIPURPOSE GELLING AGENT

Aniline
Benzaldehyde
Carbon disulphide
Carbon tetrachloride
Chloroform
Ethylene Dichloride
Ethylene glycol
Formaldehyde
o-Dichlorobenzene
Phenol
Sulphuric acid
Trichloroethylene

float to the surface. This could possibly be overcome by mixing the agent with a carrier material denser than water to ensure bottom placement. Solsberg and Parent (1986) state that liquids sinking in water can be gelled if agitated and dispersed through the water column.

Hand et al. (1978) indicate that the application of gelling agents is feasible in water up to 36-m deep. Strong currents would be a problem though there is no documentation as to the significance of currents to this technique. The gelled material could be recovered using conventional dredging techniques. This would depend on the post-deployment properties of the material which have not been ascertained at this time. Extensive development work is needed on the applicability of gelling agents to hazardous chemicals that sink.

As the Multipurpose Gelling Agent is the most promising gelling product, a brief description of its development and testing follows. The application techniques described may be of value for any powdered agents.

5.2.2 Multipurpose Gelling Agent. The Multipurpose Gelling Agent (MGA), was developed by the Calspan Corporation (Appendix A) to immobilize a broad spectrum of spilled organic and inorganic liquids in a form that could be easily removed by mechanical means. The mixture was tested on 35 hazardous compounds that were successfully gelled, with a dosage of approximately 1 kg of agent to 8 L of spilled liquid. Brugger (1980) reports compatability with 19 additional chemicals.

The formulation of MGA has been optimized based on its ability to immobilize the greatest variety of hazardous liquids with the least amount of material. To broaden the scope and universality of the gelling agent, several substitute materials were also identified. These materials met the criteria of: 1) being a dry powder with low moisture content; 2) forming viscous gels without excessive stirring or heating; and 3) a directly comparable gelling efficiency with original MGA components.

A preliminary bioassay screening test was performed on creek minnows to determine the toxicity of the MGA when used in spill control. A 1% solution resulted in a viscous solution in which the fish could barely swim. The maximum safe concentration was found to be 0.01% (by weight). The toxic effects of the gelling agent were primarily due to the thickening solution which caused suffocation and gelled the fish into the surface layer.

The MGA was initially used in powder form; however, field experiments immediately indicated several disadvantages: 1) the powder drifted away from the target under light wind conditions; and 2) the first particles to contact the spilled liquid gelled so quickly that penetration of additional agent into lower layers was prevented. To optimize the physical form, several material forms were selected: the original fine powder, powder agglomerated by water spray, a variety of tablets, crushed tablets sieve-graded into two mesh ranges, webbed dustless powder, a mat formed from the webbed powder, and a roll compressed form chipped into proper sizes.

The "roll compressed form" (produced by chipping the solid layer produced by roller-mill compression of the powder) and the two graded samples (0.5 to 2.0 mm) were determined to be the near-optimum forms. They behaved well in wind and in some liquids, they tended to sink through liquid, and they were useful with all dispersal equipment with which they were tested. The "roll compressed" form is easier to manufacture; however, the gelling efficiency of the graded forms is slightly superior.

Attempts were made to package the gel in porous bags to eliminate wind drift and simplify retrieval. Upon testing it was observed that the outer layer of gelling agent had formed a gel that protected the inner portions of the agent from contact with the liquid. The concept of packaging in porous bags was abandoned.

The MGA must be stored in moisture-proof containers at temperatures less than 50°C.

5.2.3 Deployment Techniques. Studies undertaken on the MGA included an evaluation of feasible deployment methods (Michalovic et al., 1978). Dispersal systems chosen for field evaluation worked on a variety of principles: pressurized tanks, venturi effects, centrifugal blowers, and pneumatic conveyors. Three particular off-the-shelf devices proved to be useful in the small-scale field experiments:

- a rechargeable carbon dioxide-charged dry chemical fire extinguisher;
- a venturi/compressed air system manufactured for sand blasting purposes; and

- an auger fed pneumatic conveyor such as the "Rockduster" (Mine Safety Applications - Appendix A).

Of these, the Rockduster is the most suitable for treatment of large spills. Sandblasters would be more appropriate for smaller spills.

A prototype mobile dispensing system was developed for the U.S. EPA to dispense the gelling agent. An air-cooled gasoline engine powers an auger-fed pneumatic conveyor that delivers the agent at 5.4 kg/min. through a 60-m length of 51-mm delivery hose. The system is housed in a 4-m utility trailer that can be towed by a 3/4 ton vehicle.

Most gelling agents have a specific gravity less than 1.0 and for use with sinkers, a weight-adding carrier would have to be incorporated into the mixture. No studies have been undertaken as to the feasibility of bottom application of gelling agents. Environmental conditions may prevent the required retention times for gelling which is probably not feasible under high current conditions. Removal of gelled liquid would be required.

Gelling agents are not widely available and would have to be stockpiled. Production of the MGA would require products from Dow Chemical, B.F. Goodrich, and Henley Chemicals. Producers of gelling agents include: Industrial Services International, Inc. and United States Testing Co., Inc. The MGA is estimated to cost $14.30/kg.

5.3 Granular Media Filtration

Granular media filtration is a physical separation process that removes solids from aqueous suspension as the mixture is forced (by gravity, positive pressure or a vacuum) through a series of porous media. The porous filter media is contained in a tower or column that directs the influent and effluent flows and has a method for solids removal from the filtration media, typically a backwash system. The filtration media are often layers of sand or gravel with the finer media placed on top.

Over a period of use, the filters will clog with solids material. Backflushing is required to remove the entrained matter. The backflush water, generally 1% to 4% the volume of the original filtrate, will then require disposal. Granular media filtration system capacities are generally 80 to 250 L/min · m^2.

Granular media filtration is one of the most widely used methods for separating solids from wastewater. It is most advantageous following some form of precipitation, flocculation, and/or sedimentation and may serve as an intermediate step preceding ion exchange or carbon adsorption. Specific applications include the removal of a chemical floc, such as heavy metal precipitates, following precipitation, or the removal of biological floc after secondary treatment of sanitary wastewater.

Granular media filtration, however, is ineffective in the removal of dissolved substances, produces a backwash wastewater containing a high solids concentration, and frequent backwashing is necessary when treating an influent that is high in suspended solids.

5.4 Gravity Separation Processes

Gravity separation is a physical separation process that is based on the differences in specific gravity of the various components of the liquid mixture. It functions to increase the solids concentration in a fraction of the liquid's original volume, or to separate a mixture of liquids with different specific gravities. Usually, gravity separation is used in combination with other treatment processes. Gravity separation should precede filtration whenever excessive solids are present. This will increase the length of filter cycles and provide additional protection to subsequent processes.

5.4.1 **Flotation.** Two types of flotation separation methods exist:

1) Natural: no chemical treatment or mechanical methods are necessary. Those materials less dense than water float to the surface where they can be easily removed by skimming.

2) Induced: a physicochemical treatment that causes materials heavier than water to float to the surface for easy removal. A chemical is added to create conditions conducive to the attachment of air bubbles to particles in the slurry. Costs generally make this method prohibitive for waste treatment.

   An exception to this is the EPA's mobile froth flotation unit. Compressed air is pumped into flotation chambers which creates a floating froth that contains the product to be removed. Skimmers remove the froth. The unit was designed to remove oil from beach sand following an oil spill but has also been successfully used to remove free or loosely bound creosote from contaminated river water before further treatment (Unterberg et al., 1984).

5.4.2 **Sedimentation.** Sedimentation is a necessary step following precipitation but can also be used prior to chemical treatment to remove insoluble sinking substances. The main components of a sedimentation tank are the settling tank, the influent well, and the sludge baffle. The tank is generally an open-topped pool fabricated of heavy gauge vinyl which is placed on a 5 to 8 cm sand base. A 208-L drum can serve as an influent well to reduce the velocity of the influent flow and protect the sludge layer from disturbance. The sludge baffle provides a place to withdraw the treated supernatant without removing the settled sludge.

(2)

5.4.3 Centrifugation. A centrifugal force is applied to a liquid by mechanical means resulting in the separation of its various components. Centrifugation is most applicable for the dewatering of sludges and is considered to have a high potential for removal of solids from hazardous slurries or sludges. It is not effective for the treatment of colloidal suspensions. The clarified liquid may still contain several 100 mg/L of suspended solids which will require treatment.

5.4.4 Hydrocyclone. Hydrocyclones are a form of centrifuge that separate suspended solids from a liquid. A pronounced separation of liquid contaminants is unlikely to occur, particularly those substances with specific gravity approaching 1.0. Centrifugal forces are induced by tangential fluid entry into a rotating cone assembly. The clarified effluent moves towards the centre vortex and exits through an overflow outlet while the heavier particles settle to the bottom of the cone. Hydrocyclones are employed during dredging operations and are located before the sedimentation tanks. Tests indicate that they are only effective for the removal of particles of 74 µm (sand) or larger. Hydrocyclone units are commercially available.

The hydrocyclone does not remove dissolved solids and does not completely remove suspended solids. It is only effective for the removal of particles which are the size of sand or larger. Settled solids require removal and disposal.

Cost estimates for an in-plant installation of a centrifuge are $20 to $45/ton of processed dry solids (1978).

5.5 Membrane Separation Processes

5.5.1 Reverse Osmosis. Reverse osmosis (RO) uses high pressures to force a solvent through a selectively permeable membrane. The solute is retained in 10% to 25% of the feed volume to produce an effluent with a concentration 4 to 10 times that of the original feed. This process is very effective in the removal of most dissolved organics, inorganic salts, heavy metals and emulsified oils and is used primarily in industrial applications to demineralize brackish waters and to treat a variety of industrial wastewaters. Depending on the specific waste to be treated and the type of membrane used, reverse osmosis is generally used as a final polishing step.

Reverse osmosis meets many of the requirements of a mobile treatment system: compact units are commercially available; they can be started easily and shut down relatively quickly; they can be serviced easily; they produce a small volume of concentrated waste; they do not require skilled labour; and they can be operated with electric power produced on-site.

The membrane, however, is susceptible to fouling or degradation in the presence of suspended solids, strong oxidizer, or low pH wastewaters and pretreatment is usually necessary because of this. Currently available membranes can only handle aqueous solutions and concentrated effluent must be treated or disposed of at a secure landfill.

Operation of a 227 000 L/day mobile unit would require site access, and a minimum of two technicians working 6 to 12 hours per 24 hours. Capital costs for the RO-system and support equipment are estimated at $70 000 (U.S. $, 1981). The operating costs would vary depending on the specific application.

5.5.2 **Ultrafiltration.** Ultrafiltration (UF) is also a pressure driven membrane separation process, but it operates at lower pressures than reverse osmosis. Because it is suitable for applications involving larger particles than reverse osmosis, ultrafiltration is more appropriate for hazardous chemicals, and is particularly suited to the removal of heavy metals and organics. Most full-scale uses of ultrafiltration have been in industrial operations such as the concentration of cheese whey, dye rinses, and emulsified oils. Ultrafiltration has been successfully tested for waste streams with solids concentrations of up to 46 300 ppm.

Ultrafiltration shares many of the characteristics of reverse osmosis and therefore meets most of the requirements for mobile unit application. As with reverse osmosis, ultrafiltration produces a waste stream that is four to ten times as concentrated (only 10 to 25% as voluminous) as the feed.

Ultrafiltration is not effective in the separation of low molecular weight substances. It produces low concentration permeates from high concentration wastes. Concentrated effluent must be treated and/or disposed of at a secure landfill.

Successful operation would require site access, and two technicians. A mobile unit capable of processing 227 000 L/day is estimated to cost $35 000 (U.S. $, 1981).

6 CHEMICAL TREATMENT PROCESSES

Information on chemical treatment techniques for the amelioration of hazardous chemicals that sink is provided in this chapter. Techniques that are appropriate for both in-situ and on-site applications are discussed.

Chemical countermeasures are not considered to be the best single alternative for the amelioration of soluble or insoluble sinkers (Ellis and Payne, 1983). As a group, chemical treatment techniques can be very useful in sinking hazardous spill control. Individually, however, they usually apply only to a select group of materials that can also be treated with sorbents. The greatest feasibility for chemical treatment lies in its use in conjunction with physical treatment methods (e.g., mixing with inert cover material for contaminated sediments, as discussed previously).

In-situ chemical treatment is limited to quiescent surface waterbodies with flow velocities no greater than 0.6 m/s.

6.1 Neutralization

Neutralization is the interaction of an acid and a base resulting in the formation of water, a salt and sometimes gaseous carbon dioxide. Based on fish toxicity studies it is recommended that neutralization be used as the primary treatment for all spills of acids and bases that are sufficiently large to cause a pH shift to <6 or >9. Natural dispersion of streams or ponds will dilute most chemical spills, but the consequences of not treating or overtreatment can result in chemical burns of plant life, a possible increase in the chemical oxygen demand (COD), and resolubilization of heavy metals from a lowering of pH.

Miscible sinkers subject to neutralization are listed in Table 25. Immiscible sinking chemicals that are acidic or basic in nature or that react in aqueous solution to form an acid or base are listed in Table 26.

In-situ neutralization of large spills of material is usually appropriate regardless of neutralizing agent availability. It is generally better to treat with a non-ideal agent than not at all; however, when a choice of agent is available, it is important to select the agent that produces the least toxic salt. Should several agents be available, each having a reaction product of equal toxicity, further selection should be based on both minimizing the potential for overtreatment and ease of application. As it is generally advisable to undertreat rather than risk over-treatment, weak acids and weak bases should be selected as neutralizing agents. In the event of a spill of hazardous chemical with a

TABLE 25 MISCIBLE SINKERS SUBJECT TO NEUTRALIZATION (Robinson, 1979)

Acetic acid
Acetic anhydride
Acetophenone
Acrylic acid
Aluminum chloride
Aminoethanolamine
Aniline
Benzoyl chloride
Bromine
Caustic potash solution
Caustic soda solution
Chlorosulphonic acid
Diethanolamine
Dimethylformamide
Formic acid
Hexamethylenetetramine
Hydrazine
Hydrochloric acid
Hydrofluoric acid
Hydrogen chloride
Hydrogen cyanide
Hydrogen fluoride
Maleic anhydride
Monoethanolamine
Nitrogen tetroxide
Nitric acid
Nitrosyl chloride
Oleum
Oxalic acid
Phosphoric acid
Phosphorus oxychloride
Phosphorus pentasulphide
Phosphorus trichloride
Polyphosphoric acid
Potassium hydroxide
Sodium amide
Sodium hydroxide
Sulphur monochloride
Sulphuric acid
Sulphuryl Chloride
Titanium tetrachloride
Triethanolamine
Urea

TABLE 26 IMMISCIBLE SINKERS SUBJECT TO NEUTRALIZATION (Hand et al., 1978)

Acids	
Benzoic acid	
Bases	
Calcium hydroxide	
Chemicals that React in Water to Give Bases	
Calcium carbide	Calcium hydroxide + Acetylene
Calcium oxide	Calcium hydroxide
Chemicals That React in Water to Give Acids	
Aluminum chloride	Hydrogen chloride + (Aluminum hydroxide)
Benzoyl chloride	Hydrogen chloride + Benzoic acid
Bromine	Hypobromous acid
Phthalic anhydride	Phthalic acid

specific gravity >1, a concentrated acid may be required as its similar physical characteristics would increase the probability of mixing between the spilled chemical and the neutralizing agent. For in-situ treatment, it is advisable to avoid use of solid agents whenever possible since much greater control can be obtained through use of liquid phases.

Acids and bases considered suitable for in-situ spill neutralization are listed in Table 27. The toxicity of the chemical in the event of a miss or overshoot and their cost, availability, ease of handling and effectiveness were all considered in making the recommendation. Those at the top of the list have the minimum risk of overtreatment and greatest ease of application.

TABLE 27 ACIDS AND BASES SUITABLE FOR SPILL NEUTRALIZATION (Hand et al., 1978; Akers et al., 1981)

Acids	Bases
Sodium dihydrogen phosphate	Sodium bicarbonate
Acetic acid	Calcium carbonate
Sulphuric acid	Sodium carbonate
Hydrochloric acid	

Neutralization in-situ has several inherent problems. When neutralizing a spill of an acid or base, there is always the potential for overtreatment or missing the spill plume altogether. In general, the neutralization of spills should not be attempted unless adequate monitoring equipment is available.

For water spills it is often necessary to use a precipitating agent to remove toxic metallic ions that could be evolved during the neutralization process. The precipitate would then have to be dredged or buried in place.

Significant temperature changes may result from exothermic neutralization when using concentrated solutions of treatment agents. When a dilute solution is used, the resulting smaller temperature fluctuations are generally of secondary importance. The quantity of treating agent that must be applied, however, may become extremely large. The neutralizing agent should be applied in a controlled manner to avoid sputter and the danger of serious burns. To account for any ecological damage as a result of the treatment, the temperature should be monitored throughout the neutralization process.

Depending on the characteristics of the spilled material and the neutralizing agent, some gaseous carbon dioxide may be evolved. Care must be taken to avoid personal injury and equipment damage due to subsequent frothing, bubbling or sputtering.

Both strong and weak acids and alkalis have been used for in-situ treatment of alkali and acid spills; however, their use is not well documented in the literature. Lime, limestone and soda ash have been used for acid spills, hydrochloric acid has been used for a sodium hydroxide spill and one spill of toluene diisocyanate was treated with soda ash (Ellis and Payne, 1983). No mention was made of any assessments of success or adverse side effects of the treatment. Although mixing equipment is available to ensure a rapid and complete reaction between the spilled chemical and the neutralizing agent, no case has been documented in which mixing equipment has been used.

Neutralization techniques are potential alternatives to techniques such as dredging or burial. For sunken chemicals, however, most of the techniques have not been tested in the field. A great deal of development work is needed on most of the techniques as applied to hazardous chemicals that sink.

Acids and alkalis are considered to be the most promising treatment agents for in-situ chemical countermeasures for field use (Ellis and Payne, 1983). In-situ application of sodium dihydrogen phosphate for alkali spills and sodium bicarbonate for acid spills should be developed on a pilot scale using marine craft and mechanical agitation. Experimental work is required to determine: 1) the best sensor pattern; 2) the best agitation method; 3) the best mixing method; and 4) the best choice of indicator.

6.1.1 Neutralizing Agents.

Sodium dihydrogen phosphate. Sodium dihydrogen phosphate is the chemical of choice for neutralization of bases (Unterberg et al., 1984; Ellis and Payne, 1983; Hand et al., 1978). Chemicals recommended for neutralization by sodium dihydrogen phosphate are listed in Table 28. Sodium dihydrogen phosphate is a buffer salt that maintains pH within a certain range. Neutralization in streams or ponds may or may not result in an increase in algal growth as phosphate is usually a limiting growth nutrient of aquatic flora. Misapplication would result, at most, in a pH as low as 4.5. Mistreatment with other stronger acids could cause a greater pH shift.

Sodium bicarbonate. Although calcium hydroxide is the preferred neutralizing agent for acid spills, sodium bicarbonate should be considered if pH overshoot as a result of overtreatment is to be avoided. Maximum pH due to overtreatment is 8.3, well within the fish toxicity limits of 6.0 and 9.0. Acids recommended for treatment with sodium

TABLE 28 SINKING CHEMICALS RECOMMENDED FOR NEUTRALIZATION BY SODIUM DIHYDROGEN PHOSPHATE (Solsberg and Parent, 1986)

Bases	Compounds Reacting with Water to Give Bases
Aminoethylethanolamine	Sodium
Caustic potash solution	Sodium amide
Diethynolamine	
Monoethanolemine	
Sodium hydroxide	
Triethanolamine	

bicarbonate are listed in Table 29. Sodium bicarbonate can also neutralize bases by forming carbonate ions but it is generally considered unacceptable for this purpose due to the large quantity required (Robinson, 1979).

TABLE 29 SINKING CHEMICALS RECOMMENDED FOR NEUTRALIZATION BY SODIUM BICARBONATE (Robinson, 1979)

Acids	Compounds Reacting with Water to Give Acids
Acetic acid	Acetic anhydride
Acrylic acid	Aluminum chloride
Formic acid	Benzoyl chloride
Hydrochloric acid	Bromine
Hydrofluoric acid	Chlorosulphonic acid
Hydrogen chloride	Nitrogen tetroxide
Hydrogen fluoride	Nitrosyl chloride
Nitric acid	Phosphorus oxychloride
Oxalic acid	Phosphorus pentasulphide
Phosphoric acid	Phosphorus trichloride
	Polyphosphoric acid
	Sulphur monochloride

Calcium carbonate. The maximum pH resulting from an excess application of calcium carbonate is 9.5, just over the fish toxicity limit. The use of calcium carbonate has two distinct advantages:

i) Calcium and carbonate are present naturally in surface water. Their use, therefore, does not add any foreign toxic elements.

ii) Its reaction with acid produces carbon dioxide which levitates the calcium carbonate particles thereby promoting mixing.

Calcium carbonate can be made from limestone or marble. The more finely ground the material, the faster the neutralization reaction.

Sodium carbonate. The primary disadvantage of sodium carbonate for neutralization of acid spills is that overtreatment can push the pH to 12 or greater.

6.1.2 Limitations and Availability

Neutralization using chemicals, suffers from being chemical specific and large amounts of neutralizing agent may be required. The potential for harmful effects exist; therefore, the spill dispersion must be monitored, possibly with an array of pH electrodes; and its use requires an acid/base indicator for visibility of endpoint. In flowing waters, it would probably be necessary to treat within 6 to 24 hours after the spill and should probably be completed within 12 to 36 hours (Ellis and Payne, 1983). Quiescent waters would permit a longer response time. Estuaries or tidal waters would require treatment before the next tidal reversal. Personnel must take care to avoid frothing and sputtering as a result of the evolution of gases and exothermic reactions associated with the neutralization process.

Neutralizing agents are readily available through a number of suppliers, including: A & C American Chemical Ltd., JT Baker Chemical Company, and Van Waters & Rogers. The cost of neutralizing agents is:

Sodium carbonate	\$ 264/ton (Allied Chemical)
Calcium carbonate	\$ 230/ton (Steel Brothers)
Sodium bicarbonate	\$ 940/ton (Van Waters & Rogers)
Sodium dihydrogen phosphate	\$2570/ton (Van Waters & Rogers)

6.2 Precipitate Formation

Precipitation is a physicochemical process whereby a substance in solution is transformed into a solid phase due to a change in solubility. Solubility can be affected by: 1) a change in pH of the solution; 2) a change in temperature; or 3) the addition of a substance that will react with the dissolved substance to form a less soluble product. Precipitation techniques are used in industry for the removal of heavy metals and organic colloids from waste streams and the treatment of dye manufacturing wastes. According to Hand et al. (1978), only aluminum fluoride and barium carbonate spills are likely to be successfully treated by precipitation techniques. In both these cases, toxic ions are produced that must be further treated to remove them from solution.

Very little information exists to enable estimates to be made on the speed of action and relative effectiveness of the various precipitants that are available. The optimum precipitant and dosage must be determined on a case-by-case basis by "trial-and-error" using jar tests.

In-situ precipitation has several problems. The precipitation of metallic ions can result in a buildup of material on the bottom of the watercourse. The chronic toxic effects of insoluble metal salts are presently not known. They could prove, however, to be as toxic in the long term as the spilled chemical. If the precipitate does not settle out, the colloidal material could threaten gilled species and lower the recreational and aesthetic benefits of the area. These problems can be eliminated by pumping the contaminated water and treating with precipitants, followed by sedimentation and subsequent discharge of the clean supernatant back into the environment.

There are no cases reported in the literature where in-situ precipitation techniques for sunken chemicals were utilized.

6.2.1 Precipitating Agents.

Hydroxides. Many metal ions can be precipitated with hydroxide ions supplied by sodium hydroxide, calcium hydroxide or lime. Many of the hydroxides and metals are only insoluble at pHs ranging from 8.0 to 11.0. Pretreatment to this pH will usually be necessary, making this method inappropriate for in-situ treatment. The precipitate will usually require immediate removal as the salts will re-enter the water column when the pH returns to normal. Hydroxide precipitation is therefore limited to spill treatment where the precipitate can be mechanically removed from the environment.

Sulphides. Metal ions subject to sulphide precipitation are listed in Table 30. Sulphide precipitates are usually the least soluble of the toxic metals. When heavy metal ions reach toxic concentrations, an insoluble metal sulphide will form and decrease the toxicity rapidly. The re-entry of heavy metal sulphide precipitate into the watercourse will be sufficiently small so as to minimize any secondary toxic effects, unless the sulphide is converted to an organo metallic salt. In the latter case, bacterial degradation can convert the insoluble mercuric salts to a soluble organo-mercuric compound. Akers et al. (1981), however, state that in a closed system (e.g., lakes and ponds), the insoluble metal precipitate should be removed until the chronic toxic effects of insoluble metal salts are known.

TABLE 30 METAL IONS SUBJECT TO SULPHIDE PRECIPITATION

Vanadium	Manganese	Iron
Cobalt	Nickel	Copper
Zinc	Gallium	Zirconium
Molybdenum	Ruthenium	Palladium
Silver	Cadmium	Indium
Antimony	Tantalum	Osmium
Iridium	Platinum	Gold
Mercury	Thallium	Lead
Bismuth	Polonium	Cerium
Arsenic	Praseodymium	Neodymium
Thorium	Uranium	

The difficulties with sulphide precipitation are threefold:

- the toxicity of the sulphide ion itself;
- the control of application rates to stoichiometric proportions during large spills; and
- the necessity of adding a strong base (usually sodium hydroxide (NaOH)) to increase the pH and inhibit hydrogen sulphide formation.

The literature recommends that the use of sodium sulphide precipitant be considered acceptable for use with crude controls on small spills and that its use be limited on large spills to those situations where adequate monitoring of the reaction is available.

Ten litres of water containing 0.85 kg of sodium sulphide and 0.04 kg of NaOH will treat 10 to 50 L of spill, depending on the type of heavy metal.

6.2.2 Limitations and Availability

Due to the toxicity of the sulphide ion and the difficulty in controlling the application rates, sulphide precipitation should only be considered for large spills when adequate monitoring of the reaction is possible. Since the chronic toxic effects of insoluble metal salts in waterbodies are not known, sulphide precipitates should be removed from closed systems. The solubility of the hydroxide salts increase as the pH returns to normal. Hydroxide precipitates must therefore be mechanically removed soon after treatment. The requirement for a high pH often makes hydroxides inappropriate for *in-situ* treatment. Very little information exists to enable estimates on the speed and relative effectiveness of the various precipitants available. The optimum precipitant and corresponding dosage must be determined on a case-by-case basis.

Hydroxides and sulphides are readily available. Canadian suppliers include: A & C American Chemical Ltd., and Van Waters & Rogers.

The cost of sulphides is $1240/ton (Van Waters & Rogers); and hydroxides $230/ton (Steel Brothers).

6.3 Coagulation/Flocculation

Coagulation/flocculation is a nondestructive separation process in which small suspended particles form a floc and settle out. The repulsive forces that keep the particles suspended are overcome by the addition of chemical coagulants. Gravitational and inertial forces cause the flocculated mass to settle.

The optimum coagulating/flocculating agent and the correct concentration must initially be determined by trial and error using gas tests. Gas tests determine several parameters: 1) the degree to which a substance will precipitate, the reaction time, and the required dosage; 2) the type of agents to be used and the time required to flocculate; and 3) the settling rate of the floc.

The need for controlled conditions requires that the treatment be undertaken in enclosed tanks and not in-situ. The process is non-destructive and therefore the resulting sludge is hazardous and must be collected and disposed of in an environmentally safe manner.

Various coagulating/flocculating agents are available for treating organic and inorganic suspensions. A brief description on the use of these agents follows.

6.3.1 Coagulating/Flocculating Agents.

Ferric Chloride. Dilute suspensions require dosages of 50 to 500 mg/L, although larger doses will be required for highly alkaline or concentrated suspensions. Excessive applications should be avoided as a brown-coloured effluent may result. For best results, pretreatment with lime or caustic soda may be needed to adjust the pH to above 6.0.

Alum. Dilute suspensions require dosages of 100 to 1000 mg/L; much higher dosages are necessary for alkaline and concentrated solutions. Lime or caustic may be required as a pretreatment step to adjust the pH to between 6.5 and 7.5 for optimum results.

Polyelectrolytes. Polyelectrolytes are available in three forms: anionic, cationic and non-ionic. They may be effective alone for inorganic solutions but they must be used in conjunction with another agent for organic suspensions. For dilute solutions (<100 mg/L suspended solids), cationic polyelectrolytes are added at 1 to 10 mg/L, and anionic and nonionic species are added at 1 to 100 mg/L.

6.3.2 Limitations and Availability.

Ferric chloride is extremely corrosive and must be stored and transported in special corrosion resistant containers. Dosages are not stoichiometric and dry ferric chloride must be dissolved before use. Ferric chloride is readily available in dry or liquid form. Liquid form is available in 11.4 to 15 m^3 bulk truckload lots, 15 to 38 m^3 carloads, or 19 to 49-L carboys. Van Waters & Rogers supply ferric chloride at a cost of $4500/ton.

Alum solution is also corrosive, dosages are not stoichiometric, and the resulting sludge is voluminous and difficult to dewater. Solid alum is available in lumps, in ground, rice, or powdered form. Shipments may be in 45-kg bags, in drums or in bulk quantities (over 1800 kg). Solutions up to 50% are available in minimum loads of 15 m^3. Alum is supplied by A & C American Chemical and Van Waters & Rogers and can be purchased for $295/ton (Allied).

Stock polymers can be very viscous. Surfaces contacting these solutions should be materials such as stainless steel and over-dosage can sometimes work against the treatment process. Polyelectrolytes are available in dry or liquid form. Dry polymers are supplied in 45-kg bags or barrels.

6.4 Solvent Extraction

Solvent extraction is a separation process whereby a substance is removed from the water with a liquid carrier. The liquid carrier is generally a dilute acid or base.

Liquid-liquid extraction can be used to remove organics from aqueous wastes. Current applications include the extraction and recovery of phenols, oils, and organic acids. Post-treatment is always necessary. Due to the difficulties in recovering the contaminated solvent, in-situ treatment is not recommended. On-site extraction is possible, however, by pumping the contaminated water into treatment tanks. Care must be taken in selecting a solvent that has a relatively low aqueous solubility, is relatively non-polar, is nontoxic, has a high partition coeficient, is easily separated from water, and is easy to handle.

Only moderate removal of the contaminant may occur using solvent extraction, necessitating further treatment. Solvent extraction cannot be used in-situ and solvents must be recovered and treated to remove the contaminants. No commercial mobile units are available.

6.5 Polymerization

Polymerization is the in-situ catalysis of a free-radical addition reaction of a released monomer. It serves to reduce the mobility of the hazardous material and facilitates subsequent removal.

Studies have been conducted to determine the feasibility of using subsurface injection techniques to polymerize a spill (Unterberg et al., 1984). In general, it is difficult to obtain rapid polymerization under ambient conditions typical of real spill situations. The process requires an elaborate subsurface injection system that is considered to be dangerous to implement under field conditions. In-situ polymerization is not recommended until the technique is further refined.

6.6 Oxidation/Reduction

Oxidation/reduction reactions are chemical reactions in which the oxidation state of one reactant is raised (the oxidant) while that of the other is lowered (the reductant). The complete oxidation of an organic substance results in the formation of carbon dioxide, water, insoluble organics, and partially oxidized organics. The latter two may require further treatment such as carbon adsorption or sedimentation. The detoxification of a hazardous substance is a direct result of the change in valence state or the consequent destruction of chemical bonds. Sinking hazardous chemicals that are amenable to in-situ oxidation are listed in Table 31.

TABLE 31 SINKING HAZARDOUS CHEMICALS AMENABLE TO IN-SITU OXIDATION (Hand et al., 1978)

cresols
2, 4-dinitroaniline
2, 4-dinitrophenol
diphenylmethanediisocyanate
phenol
phthalic anhydride
trichlorophenol

Aeration techniques supplemented with oxygen and/or ozone, are recommended as these oxidants produce nontoxic reaction products only. Other oxidizing agents are recommended for in-situ use only as a last resort and only if the spills are completely contained. Problems include:

- production of toxic intermediary reaction products;
- slow and incomplete oxidation reactions (to overcome this it is necessary to overtreat to such an extent that severe toxic conditions are produced by the treatment agent); and
- nonspecific oxidizing agents which react with most organic materials; oxidation of natural organic material in the environment will accompany oxidation of the spilled material, thereby upsetting the ecological balance; oxidizing agents have not been used extensively for the detoxification of hazardous materials except in aerated lagoons and other closed systems where the reaction can be completely controlled.

6.6.1 Oxidizing Agents.

Oxygen. Oxygen can be applied through aeration techniques that may or may not be supplemented with pure oxygen. Aeration can be accomplished with use of aerators produced for the waste management industry or by using the discharge stream of a hydraulic dredge. Oxygen can be applied by vapourization of liquid oxygen or injection of air into the discharge pipe with a compressor. The primary advantage of aeration techniques is that no toxic substances are introduced in the process. Additional benefits include the precipitation of ferrous iron, the oxidation of sulphites and hydrogen sulphide, and the stripping of volatile materials from wastewaters.

Ozone. Ozone oxygenation has been used in the waste treatment field for the destruction of phenolics, cyanides, PCBs, water insoluble organics, biodegradable organics and certain polyorganic chemicals. While ozone is one of the strongest oxidizing agents known to man, toxic byproducts such as ketones, organic acids, perocids, expocids, sulphones, sulphoxides and other oxygenated species may be produced (Unterberg et al., 1984).

Ozone generating equipment can produce 1 to 6% ozone from a feed stream of air or pure oxygen. Ozone is an unstable gas and decomposes to oxygen at pressures in excess of 207 kPa (30 psi). Due to its instability, ozone must be generated on-site. An ozonolysis unit capable of producing 270 m^3/day is estimated at costing \$285 000 (U.S. \$, 1981). Ozone treatment is generally used as a final polishing step because of the high capital costs associated with an ozonolysis unit. At present, no commercial mobile units are available for emergency response. It should be noted that ozone has a significant inhalation toxicity.

Potassium permanganate. Potassium permanganate, a relatively strong oxidizing agent, will oxidize aldehydes, phenols, mercaptans and unsaturated acids. Because of its purple colour, control of the concentration and oxidation reaction can be achieved visually. The products of oxidation include carbon dioxide, potassium hydroxide and insoluble manganese dioxide. Manganese dioxide is toxic and must be removed after treatment.

Hydrogen peroxide. Hydrogen peroxide will oxidize sulphides, mercaptans, amines, phenols, and cyanides. Metal salts (particularly iron salts) or metals (aluminum, copper, chromium) must be present to catalyze the reaction. Hydrogen peroxide does not introduce any foreign ions into the waterway.

Chlorine. As an oxidant, chlorine is usually applied as sodium hypochlorite or calcium hypochlorite. Both are effective in oxidizing cyanides, nitriles, aliphatic amines and phenolic compounds. Free chlorine is a product of the oxidation reaction and must be removed by further treatment. In many cases an alkaline pH is required to ensure a complete reaction (e.g., when treating phenols) or to prevent the formation of toxic reaction products (e.g., when treating cyanides).

6.6.2 Limitations and Availability

Use of oxidizing agents in-situ is discouraged for several reasons: the oxidants are toxic, even at low concentration; the reactions are slow; the products are not easily controlled and often toxic; and overtreatment is likely when attempts are made to speed the reaction.

Oxidizing agents may react violently in the presence of significant quantities of readily oxidizable organics. Therefore these agents should be well mixed and added slowly to spills to prevent violent reactions.

Waste solutions to be treated by chemical oxidation must be pH adjusted to ensure efficient oxidation. This requirement can limit the applicability of oxidation in a spill situation where immediate response and limited control makes preparation of the spill site difficult.

Oxidizing agents should only be used in closed systems where the reaction can be completely controlled.

All oxidants previously discussed are readily available from CIL Inc., Dow Chemical, Van Waters & Rogers, and FMC of Canada.

Costs for oxidants are: Potassium permanganate, $4150/ton (Van Waters & Rogers); Hydrogen peroxide, $720/ton (50%) (FMC); and Chlorine, $450/ton (Van Waters & Rogers).

6.7 Biological Treatment

Biological treatment is a natural means of removal of organic substances through biochemical transformation processes. The biodegradable hazardous substance is brought into contact with mixtures of organisms or microbial enzymes that degrade it to an innocuous substance. For a hazardous material to be considered for treatment it must: 1) be biodegradable, 2) be an organic compound containing no metals, and 3) not be critically toxic or gaseous, necessitating immediate removal. The potential effectiveness of treatment of various materials are summarized in Table 32.

Due to the time and degree of control required, in-situ biological treatment has limited potential as an emergency response measure. It can, however, be used in areas inaccessible to other methods of treatment, at minimum cost and effort. Biological treatment is best utilized as a supplemental tool to other methods of spill treatment.

Biodegradation as an emergency response measure suffers from several difficulties:

1) many hazardous materials are resistant to biodegradation;
2) the effectiveness of biological treatment is dependent on several variables that cannot be controlled;
3) if using cultures from sewage treatment plant operations, pathogenic bacteria may be introduced into the waterway; and
4) to proceed at a rapid rate, large quantities of acclimated cultures are needed.

Hazardous organic substances that tend to be resistant to biodegradation are those with complex chemical structures (e.g., aromatics and fully halogenated aliphatics). High organic concentration, low solubility and high molecular weight also hinder biodegradation (Unterberg et al., 1984).

The growth of the bacteria in a particular situation will be a function of the culture viability, length of the lag phase, acclimation, growth requirement, temperature, oxygen availability, type of substrate, surface availability and contact time (Akers et al., 1981).

Oxygen, essential to biodegradation, will be depleted upon addition of the microorganisms. Not only will this inhibit biodegradation but it could prove to be detrimental to the existing biota. Natural aeration may prove to be inadequate, requiring that supplemental oxygen be provided with mechanical aerators.

TABLE 32 BIOLOGICAL TREATMENT (Akers et al., 1981)

Chemical	% Oxidation	Seed	Test Duration
a. **Biological Oxidation** (treatment plant conditions)			
Chlorobenzene	17.1	ASS	192 hours
Formaldehyde	99	ASS	120 hours
Cresols	28.4 to 36.6*	ASS	192 hours
Phenol	34*	ASS	192 hours
Phenol	39**	ASS	12 hours
b. **Biological Oxidation** (quiescent conditions)			
Formaldehyde (500 ppm)	47	AAS	5 days
Formaldehyde (333ppm)	94	AAS	5 days
Furfural	100	AAS	2 days
Benzoic Acid	46	SS	10 days
Formic acid	40	ASS	5 days
Cresols	95 to 100	SS	2 to 7 days
Benzonitrile	40	SS	5 days
Potassium cyanide	0	ASS	7 days

c. **Reported Organic Compounds Resistant to Removal**

Compound	Technique
Dioxane	BOD ASS
Ethylene chlorohydrin	BOD ASS
2-Hydroxybutanol	BOD ASS
2,2-Oxydiethanol	BOS ASS
Tetraethylene glycol	BOD ASS
Thioglycolic acid	Resp ASS
Triethanolamine	BOD ASS

*	acclimated to aniline	resp	respirometer
**	acclimated to phenol	AAS	acclimated sludge seed
SS	sewage seed	ASS	activated sludge seed

Biodegradation is highly dependent upon temperature. Temperature will affect the acclimation of the bacteria, the rate of bacterial growth and the effectiveness of treatment (Akers et al., 1981). Decreased metabolic rates at low temperatures could have serious adverse effects on the effectiveness of biological treatment. In general, the optimum temperature is in the range of 15° to 35°C.

Bacteria useful in oxidation of hazardous materials include natural cultures in soil and surface waters, activated sewage sludge, and special strains that have been developed commercially. It is entirely possible that the spill of hazardous material will destroy the natural microbial population and acclimated cultures will be required. If using activated sewage sludge, care must be taken to ensure that no pathogens are introduced into the waterway. To date, several organisms have been successfully cultured and used to degrade a variety of organic chemicals in both the laboratory and pilot-scale experiments. The bacteria *Pseudomonas* has been found to be the most versatile, degrading a broad spectrum of toxic materials. *Pseudomonas* is relatively easy to produce in large volumes. It is stated in the literature that no toxic or noxious sludges result from the degradation process; however, data on long-term effects of biodegradation (toxicity of by-products and bioamplification) are not available. Dried bacterial cultures are used for oil spills; however, no rate data is available. It should be noted that freshwater cultures might not be useful in marine and coastal waters as high salinities decrease the effective pH range.

Bacteria can be stored for long periods of time in the dormant state (frozen, lyophilized powder or liquid). Storage in lyophilized form is advantageous since the bacteria can be kept at room temperature; however, reconstitution requires several hours preparation time. Liquid form is desirable because the bacteria are ready for immediate application. Cultures could be deployed easily and rapidly by spraying from a helicopter, shore or boat. Armstrong (Hand et al., 1978) notes that some bacteria strains will tend to sink themselves. Those that do not could be placed in sinkable bags.

The activated sludge process is one of the most widely used biological wastewater treatment processes. Ghassemi et al. (1981) evaluated UNOX and OASES (two high purity oxygen activated sludge processes) for use in mobile waste treatment units. Several key limitations were identified: unsuitability for handling toxic waste, long startup and stabilization period, susceptibility to "shock" loads, unsuitability for treatment of waters containing volatile hydrocarbons, the requirement for trained operating personnel, and the requirement for a large reactor size to handle concentrated wastes. It was determined that the largest mobile reactor (47 300 L), at a retention time of 48 hours, would have a hydraulic capacity of only 23.65 m^3/day. Capital costs for a unit capable of processing 227 m^3/day were estimated to be $200 000 (1982).

In-situ treatment of organics is recommended only if: the spill is completely contained; there is sufficient time available for biodegradation; and the introduction of microbes will not be detrimental to the existing environment. Rapid dispersion may make biological treatment totally impractical. Mobile units have a relatively low hydraulic capacity.

6.8 Dispersion/Dilution

Dispersion/dilution is a process that facilitates dilution of a hazardous substance by promoting the dispersion of the hazardous substance. The principle behind the use of dispersion is to spread the material over a larger area to reduce the concentration to below toxic limits. With some organic pollutants (e.g., oil) this can also increase the biodegradation rate. Whether by chemical or mechanical means, dispersion should not be considered as a first choice response to any hazardous material spill. Dispersion techniques should only be used when all other amelioration techniques have been eliminated from consideration. Chemicals listed in the Chemical Hazards Response Information System (CHRIS) that are possible candidates for dispersion in selected instances are listed in Table 33 (Hand et al., 1978).

TABLE 33 CHEMICAL HAZARDS RESPONSE INFORMATION SYSTEM (CHRIS) CHEMICALS SUBJECT TO DISPERSION (Hand et al., 1978)

Aniline
Benzoyl chloride
Bromine
Calcium carbide
Calcium oxide
Carbolic oil
Cresols
Dichloromethane
2,4-Dichlorophenol
Dimethyl sulphate
Epichlorhydrin
Furfural
Lithium aluminum hydride
Toxaphene

Whether dilution is acceptable is determined by the use of the waterbody (fishing, bathing, navigation), its nature (flowing stream, open sea), and its size as well as the nature and size of the spill. Scenarios where dispersion might be appropriate are:

i) In open water where natural dispersion may result in rapid dilution of the spilled chemical.

ii) In small streams flowing into large rivers. The greater flow should result in quick dilution.

iii) At the mouth of a harbour that experiences fast tidal currents. Dispersants should be applied on an outgoing tide.

Dispersion can be achieved by mechanical and chemical means. It should be noted that the only large-scale field testing of dispersion techniques has been in the area of oil spills. The technology for application of these techniques to spills of sinking chemicals is not well developed.

6.8.1 Mechanical Dispersion. A number of mechanical devices are available for dispersion; however, their success would depend on the size and location of the spill as well as the depth of the watercourse. Propwash from a boat and water streams from a hose could be effective in shallow areas for small spills. The use of commercially available aerators to disperse materials from the bottom of the watercourse could also be effective. For spills greater than 400 kg, it is felt that the degree of mixing to be achieved is so large that the use of mixing equipment does not seem feasible (Srinivasan et al., 1975).

Flow augmentation using water stored upstream from a spill could be effective in small streams flowing into large rivers. Some means must be available for predicting flow rates and the duration of the toxic concentrations in the waterbody.

The effective use of mechanical dispersion devices is limited to relatively small spills in shallow areas. Due to the degree of mixing required, mechanical dispersion is not recommended for spills larger than 400 kg. Flow augmentation requires the availability of stored upstream water. This method is only appropriate for small rivers of relatively low flow. Some method must be available for determining flow rates and the duration of toxic concentrations. Because of the potential toxic effects on the aquatic biota, dispersion should never be considered as a first choice response.

6.8.2 Chemical Dispersion. Chemical dispersion facilitates the dilution of a hazardous chemical through the use of surfactants. Surfactants lower the surface tension at the interface between the water and the chemical resulting in a lateral dispersion of the chemical over the surface of the waterbody. The increased surface area dilutes the chemical and promotes bacterial degradation.

Application of dispersants is generally achieved through use of hand operated pumps and pressure units, portable pump eductor systems, spray booms and aerial spray methods. Mixing may be necessary to aid dispersion. This could be accomplished using the propwash of a boat.

Chemical dispersion methods have not been developed for use on spills of sinking hazardous materials. No dispersion formulation for chemicals that sink is presently available.

6.9 Application of In-situ Chemical Countermeasures

In-situ chemical treatment requires that the treatment chemical and the hazardous material be brought into intimate contact to ensure that the countermeasure is effective. For the treatment of sinking chemicals the treatment agent can be added: 1) in close proximity to the bottom of the watercourse, or 2) directly to the water surface. In quiescent waters mechanical agitation would be required to promote mixing of the spilled chemical and the treating agent. Containment of the spill would enhance the treatment efficiency and minimize the potential of any secondary effects of the reaction.

6.9.1 Application. Application of the chemical can be made with a dry powder, with a slurry of powder in water, or with a liquid solution. For in-situ treatment, it is advisable to avoid the use of solid agents whenever possible since much greater control can be achieved through use of liquid phases.

Surface application of the chemical can be made from a mobile marine vessel or from an aircraft. The advantages of aircraft over mobile marine vessels is that they can be rapidly deployed to the spill site and the transportation of the chemical to the water site may be avoided. This apparent efficiency is somewhat offset by the low carrying capacity relative to marine vessels and the difficulty in achieving precise dumping.

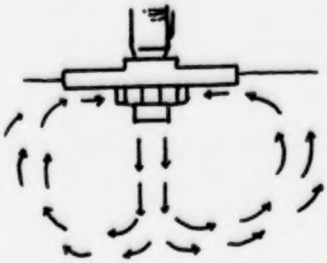
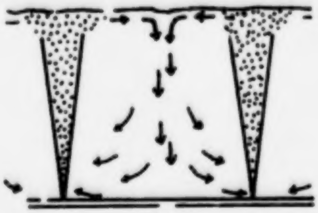
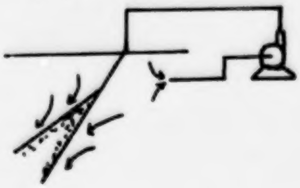
The application of powder dumps from aircraft is considered to be feasible for localized spills when the time element is critical. Outfitting the aircraft with equipment to prepare or dispense slurries or solutions would be relatively easy since this technique is already used in agriculture. The required mixing of the dispersant/contaminant is then a problem to overcome.

Surface application of chemical-treating agents should utilize the agent in slurry or solution form. The liquid can be dispersed with a mechanical agitator or by injecting it into the suction side of the pump for a liquid jet system.

For treatment of insoluble sinkers the chemical agent would be best applied in close proximity to the bottom of the waterbody. To avoid overdosing or misapplication, small spills should be dyked and the agent applied directly. For treating spills of medium to large size, the treating agent could be applied with an inert covering material to form an active cover. The solution could be pressure injected into the discharge pipe of the dredge being used to place the covering material.

6.9.2 Mixing. Mixing, especially in the treatment of sinking chemicals, would greatly promote the rate of reaction between the spilled material and the treatment agent. The mixing of material is presently carried out by mechanical agitation, gas-liquid agitation, or liquid-liquid agitation. These processes are summarized in Table 34.

TABLE 34 SUMMARY OF MIXING TECHNIQUES (Ellis and Payne, 1983)

	Characteristics	Advantages
Mechanical Agitation 	- agitator - motor systems; standard sizes 1.5 to 75 kW - 12 m zone of complete mixing in 1.8 m depth with 2.2 kW pump, falls to 6 m with 0.7 kW pump - power requirement 2.6 to 7W/m^3 for liquid blending, power/unit volume increased by a factor of 10 for solids suspension	- easy to install in the field
Gas-Liquid Agitation 	- systems are usually designed for specific situations - typical airflows per station range from 0.002 to 0.01 m^3/s at 3 m apart	- bubble curtain may help prevent further dispersion of spill - more energy efficient than mechanical in depths greater than 3.7 m - oxygenates water
Liquid-Liquid Agitation 	- a liquid jet system could be operated from a marine craft moving over the spill area	- may bring the treatment chemical and the hazardous material to the water surface

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APPENDIX A

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(514) 697-9210

Andesite of California, Inc.
1260 South Goodrich Boulevard
Los Angeles, California 90022
USA
Ph: (213) 726-7602

B.F. Goodrich Canada Limited
521 King Street West
Kitchener, Ontario
Canada N2G 1C5
Ph: (519) 888-4300

Calgon Canada Inc.
27 Finley Road
Bramalea, Ontario
L6T 1B2
Ph: (416) 457-5310

Calspan Corporation
Environmental Systems Dept.
P.O. Box 400
Buffalo, New York 14225

CIL Inc.
CIL House 90
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North York, Ontario
M2H 6H2
Ph: (416) 229-7000

Dow Chemical Canada Inc.
Modeland Road
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N7T 7K7
Ph: (519) 339-3131

FMC of Canada Ltd.
Industrial Chemicals Division
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Ph: (604) 685-6508

Hercules Canada Inc.
Mississauga Executive Centre
4 Robert Speck Parkway
Mississauga, Ontario
L4Z 1S1
Ph: (406) 848-1800

Industrial Services International Inc.
P.O. Box 10834
Bradenton, Florida 33507
USA
Ph: (813) 792-7778

J.T. Baker Chemical Company
2 Norelco Drive
Weston, Ontario
M9L 1R9
Ph: (416) 749-8620

Kelco, Division of Merck & Co., Inc.
75 Terminal Avenue
Clark, New Jersey 07066
USA
Ph: (201) 381-6900

Lexcan Industrial Supply Limited
85 Vulcan Street
Rexdale, Ontario
L1A 1A1
Ph: (416) 249-8361

Mine Safety Applications (MSA) Co.
of Canada Ltd.
148 Norfinch Street
Downsview, Ontario
M3N 1X8

National Car Rental System, Inc.
Mud Cat Division
P.O. Box 16247
St. Louis Park
Minnesota 55416
USA
Ph: (612) 893-6400

Penta Ocean Construction Co., Ltd.
2-8, Koraku 2 Chome
Bunkyo-Ku
Tokyo, 112
Japan

Rohm & Haas Canada Ltd.
2 Manse Road
West Hill, Ontario
Ph: (416) 364-3234

Sea Clean Inc.
7000 SW 62 Avenue, Suite 555
Miami, Florida 33143
USA

Schlegel Lining Technology Inc.
P.O. Box 9115, Station "F"
Calgary, Alberta
T2J 5S7
Ph: (403) 273-3066

Sorbent Products Co., Inc.
Maplewood, New Jersey
Ph: (201) 762-4705

Steel Brothers Canada Ltd.
4836 - 6th Street, NE
Calgary, Alberta
(403) 276-9335

Takenaka Komuten Co., Ltd.
21-1, 8-Chome
Ginza, 20C8UO-Ko
Tokyo, Japan
Ph: (03) 542-7100

Terra Nova Power & Development Ltd.
36 Pippy Place, P.O. Box 13531
St. John's, Newfoundland
A1B 4B8
Ph: (709) 753-9043

3M Canada Inc.
London, Ontario
P.O. Box 5757
N6A 4T1

Toyo Construction Co. Ltd.
7-1, Kanda-Nishikicho
3-Chome, Chiyoda-Ku
Tokyo, Japan

United States Testing Co., Inc.
Environmental Sciences Division
1415 Park Avenue
Hoboken, New Jersey 07030
USA
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Van Waters & Rogers
9800 Van Horne Way
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V6X 1W5
Ph: (604) 273-1441

Selected Dredging Companies:

Argyle Co. Ltd.
650 Hudson
Montreal, Quebec
H4X 1X3
(514) 488-6241

Beaver Marine Construction
Division Beaver Construction
Group Ltd.
P.O. Box 1447 H.N.P.S.
Halifax, Nova Scotia
B3K 5H7

Canadian Dredge & Dock Inc., Ltd.
60 Harbour Street
Toronto, Ontario
M5J 1B8

Cartier-McNamara Corp.
P.O. Box 418
Whitby, Ontario
L1N 5S4

Dean Construction Co., Ltd.
Box 3216
Tecumseh, Ontario
N8N 2M4

Dillingham Construction Ltd.
20 Brooksbank Avenue
North Vancouver, B.C.
V7J 2B8

Dragage St-Maurice Ltée.
84 Rang de l'Île
Notre Dame de Pierreville, Québec
J0G 1G0
(514) 568-2806

Northern Construction Company Ltd.
1304 Hornby Street
Vancouver, B.C.
V6Z 1W6

Pitts Engineering Construction
Division of Banister Continental Ltd.
7500 Woodbine Avenue
Markham, Ontario
L3R 4M8

Sceptre Dredging Ltd.
1000 de Serigny
Longueuil, Québec
J4K 5B1
(514) 463-0590

Sceptre Riedel Dawson Constructors Ltd.
14400 River Road
Richmond, B.C.
V6C 1L3

Standard Dredging Co.
St. John, New Brunswick

APPENDIX B

PRODUCT DATA SHEETS FOR PHYSICAL TREATMENT PROCESSES

APPENDIX B PRODUCT DATA SHEETS FOR PHYSICAL TREATMENT PROCESSES

PRODUCT: 3M Oil Absorbent **TYPE:** Sorbent

DESCRIPTION: 3M Oil Absorbent is an inert entangled mass of fine polypropylene fibres. It is oleophilic and hydrophobic.

PHYSICAL SPECIFICATIONS:

Available Geometry:	Rolls (0.9 x 0.46 m) Sweeps (0.48 x 0.3 m) Sheets (0.0 x 0.9 x 0.1 m) Particulate Pillows (0.36 x 0.63 m) Booms (0.2 x 3 m)
Specific Gravity:	0.043
Shelf Life:	Indefinite
Storage Requirement:	Protect from UV rays

OPERATING SPECIFICATIONS:

Toxicity:	Nontoxic
Disposal:	Incineration (<0.01% ash)
Regeneration:	Wring out - 20 cycles

STATUS OF DEVELOPMENT & USAGE: Commercial product used for the cleanup of oil spills. Compatibility with a wide range of hazardous chemicals reported.

PERFORMANCE:

Compatibility:	
Capacity:	13 to 25 times its weight
Cost:	$122.35/bale (100 sheets 0.46 x 0.46 x 0.01 m)

AVAILABILITY & COMMERCIAL INFORMATION:

Manufacturer:

Occupational Health & Safety Products
3M Canada Inc.
P.O. Box 5757
London, Ontario
N6A 4T1

Distributor:

ANCO Chemicals Limited
P.O. Box 400
Maple, Ontario
L0J 1E0
Ph: (406) 832-2276

PRODUCT: SSC Sorbent **TYPE:** Sorbent

DESCRIPTION: A synthetic sorbent made of polyurethane.

PHYSICAL SPECIFICATIONS:

Available Geometry:	Boom (2.4 m, 0.2 m dia.) Sheets (0.3 x 1.8 x 0.04 m) Strips (0.35 x 0.02 x 0.01 m) Pillow (0.13 m^3)
Specific Gravity:	< 1.0
Shelf Life:	Indefinite
Storage Requirements:	None

OPERATING SPECIFICATIONS:

Toxicity:	Nontoxic
Disposal:	Recycled, landfill, or incinerate
Regeneration:	Wring out

STATUS OF DEVELOPMENT & USAGE: Commercial product for cleanup of oil spills. Compatability with some hazardous chemicals.

PERFORMANCE:

Compatability:
- Cresols
- PCBs
- Formaldehyde
- Chloroform
- Aniline
- Nitric acid
- Carbon tetrachloride
- Carbon disulphide
- Cyanogen chloride
- Hydrochloric acid
- Phosphoric acid

AVAILABILITY & COMMERCIAL INFORMATION:
Manufacturer:

Spill Control Company
828 North Grand Avenue
Covina, California 91724
Ph: (213) 339-1259

PRODUCT: Safestep Sorbent	**TYPE:** Sorbent

DESCRIPTION: An inert, inorganic particulate sorbent, composed of silicones and other minerals. Insoluble in most solvents and strong mineral acids.

PHYSICAL SPECIFICATIONS:

Available geometry:	0.03 mm particles in 11 kg bags
Shelf Life:	Indefinite

OPERATING SPECIFICATIONS:

Toxicity:	Nontoxic
Disposal:	Incineration or landfill
Regeneration:	Cannot regenerate

STATUS OF DEVELOPMENT & USAGE: Commercial product developed for the treatment of hazardous material spills. Documentation of usage not obtained.

PERFORMANCE:

Compatability:	Petro-chemicals, acids and caustics, organics and inorganics, PCBs.

AVAILABILITY & COMMERCIAL INFORMATION:
Manufacturer:

Andesite of California
1260 South Goodrich Boulevard
Los Angeles, California 90022
Ph: (213) 726-7602

PRODUCT: Conwed D Sorbent Pads **TYPE:** Sorbent

DECRIPTION: A slightly abrasive, low density polymeric foam pad for the absorption and retention of spilled oil and chemicals.

PHYSICAL SPECIFICATIONS:

Available Geometry:	Pads (0.5 x 0.5 x 0.006 m)
Specific Gravity:	0.04
Shelf Life:	Indefinite
Storage Requirements:	Temperature cannot exceed 77°C

OPERATIONAL SPECIFICATIONS:

Toxicity:	Nontoxic
Disposal:	Incineration
Regeneration:	Wring out product

STATUS OF DEVELOPMENT AND USAGE: Commercial product used in oil spill cleanup. No documentation of use on hazardous materials.

PERFORMANCE:

Compatability:

- Aniline
- Benzonitrile
- Carbon bisulphide
- Carbon tetrachloride
- Chlorobenzene
- Chloroform
- Cresol
- Malathion
- Nitrobenzene
- Perchloroethylene
- Tetraethyl lead
- Trichloroethane

Capacity:	up to 23x its weight in petroleum products
Cost:	$95/carton (80 pads/carton)

AVAILABILITY & COMMERCIAL INFORMATION:

Manufacturer:

Conwed Corporation
Sorbent Products
332 Minnesota Street
P.O. Box 43237
St. Paul, MI 55164
Ph: (612) 221-1144

Distributor:

Sorbco
5369 Maingate Drive
Mississauga, Ontario
L4W 1G3
Ph: (416) 624-1264

PRODUCT: Imbiber Beads **TYPE:** Sorbent

DESCRIPTION: Cross-linked copolymer spheres that absorb a variety of organic liquids and many polar compounds. Imbiber beads do not absorb water, solids, high viscosity oils, low molecular weight alcohols, glycols, acetic acid, acetonitrile, nitromethane and other highly polar chemicals.

PHYSICAL SPECIFICATIONS:

Available Geometry:	Beads, packets, blankets
Specific Gravity:	Varies from 0.95 to >1.0
Shelf Life:	Indefinite
Storage Requirement:	None

OPERATING SPECIFICATIONS:

Toxicity:	Nontoxic
Disposal:	Depends on chemical imbibed

STATUS OF DEVELOPMENT & USAGE: Commercially available as absorbent blankets and valves for storage tanks. They are an important constituent of EPA's Multipurpose Gelling Agent (MGA).

PERFORMANCE:

Compatability:	
Capacity:	Varies but can be up to 27 x bead volume
Cost:	$35.20/kg (powder)

AVAILABILITY & COMMERCIAL INFORMATION:

Manufacturer:

EMCO Inc.
1015 Louisiana Street
Little Rock, AR 72207
Ph: (501) 374-7878

Distributors:

ANCO Chemical Co. Ltd.
85 Malmo Court
Maple, Ontario
Ph: (406) 832-2277

ANCO Chemical Co. Ltd.
6905 Hebert Street
Laprairie County
Ville Ste-Catherine
J0L 1E0
Tel: (514) 632-0950

PRODUCT: Conwed Sorbent Blanket
TYPE: Sorbent

DESCRIPTION: A water resistant mat of natural fibres reinforced with polypropylene mesh.

PHYSICAL SPECIFICATIONS:
Available Geometry: Rolls (0.9 x 6.1 m)
Specific Gravity: 0.06
Shelf Life: Indefinite
Storage Requirements: Away from elements and sunlight

OPERATIONAL SPECIFICATIONS:
Toxicity: Nontoxic
Disposal: Landfill, incineration
Regeneration: Not reusable

PERFORMANCE:
Compatability:
Capacity: Oil: 12 to 14 times its weight
Cost: $145/roll

AVAILABILITY & COMMERCIAL INFORMATION:

Manufacturer:

Conwed Corporation
Sorbent Products Division
332 Minnesota Street
P.O. Box 43237
St. Paul, MI 55164
Ph: (612) 221-1144

Distributor:

CIL Inc.
P.O. Box 836
Edmonton, Alberta
T5J 2L4
Ph: (403) 465-0221

PRODUCT: Diasorb **TYPE:** Sorbent

DESCRIPTION: A light, porous, inert, inorganic, sodium silicate material.

PHYSICAL SPECIFICATIONS:
Available Geometry: Spheroid granules 8 to 200 mesh
Specific Gravity: 0.035
Shelf Life: Indefinite

OPERATIONAL SPECIFICATIONS:
Toxicity: Low
Disposal: Will not burn

STATUS OF DEVELOPMENT AND USAGE: Commercial product developed as a universal absorbent for hazardous materials.

PERFORMANCE:
Compatability: Nitric acid, Phosphoric acid, Formaldehyde, Phenol, Ferric chloride, Chlorosulphonic acid
Capacity: Generally > 10 L/kg of Diasorb

AVAILABILITY & COMMERCIAL INFORMATION:
Manufacturer:

Soda Products Division
Diamond Shamrock Corporation
1100 Superior Avenue
Cleveland, Ohio 44114
Ph: (216) 694-4500

PRODUCT: SPC Oil Sorbent **TYPE:** Sorbent

DESCRIPTION: A synthetic sorbent formed of melt blown non-woven fibres of polypropylene.

PHYSICAL SPECIFICATIONS:

Available Geometry:	pads, booms, sweeps, blanket, pillows, particulate
Specific Gravity:	<1.0
Shelf Life:	Indefinite
Store Requirements:	Unspecified

OPERATIONAL SPECIFICATIONS:

Toxicity:	Nontoxic
Disposal:	Incineration (<0.1% ash)
Regeneration:	Squeezing or "wringing" out

STATUS OF DEVELOPMENT AND USAGE: Commercial product for mitigation of oil spills. Company literature claims compatability with a number of hazardous chemicals.

PERFORMANCE:

Compatability:	
Capacity:	Oil: 10 to 20 times its weight

AVAILABILITY & COMMERCIAL INFORMATION:
Manufacturer:

Sorbent Products Co., Inc.
Maplewood, New Jersey
Ph: (201) 762-4702

PRODUCT: Multipurpose Gelling Agent **TYPE:** Gelling Agent

DESCRIPTION: A formulation of four polymers fluidized with fumed silica for the immobilization of aqueous liquids, chlorinated organics, alcohols and non-polar hydrocarbons.

OPERATING PRINCIPLE: Each individual component selectively interacts with the spilled chemicals to create an immobile gel that can be removed by mechanical means (i.e., dredging).

PHYSICAL SPECIFICATIONS:

Composition:	5% Gelgard (Dow) 30% Imbiber Beads (Dow) 30% Hycar 1422 (BF Goodrich) 25% Carbopol 934 (BF Goodrich) 10% Fumed Silica
Available Geometry:	Powder fluidized in fumed silica
Specific Gravity:	<1.0
Shelf Life:	Indefinite
Storage requirements:	Must be kept dry

OPERATING SPECIFICATIONS:

Toxicity:	Max. safe concentration is .01% by weight
Regeneration:	Cannot be regenerated

STATUS OF DEVELOPMENT & USAGE: MGA was developed for the EPA by the Calspan Corporation under EPA contracts 68-01-0110 and 68-01-2093.

PERFORMANCE:

Compatability:

- Aniline
- Benzaldehyde
- Carbon disulphide
- Carbon tetrachloride
- Chloroform
- Phenol
- Formaldehyde
- o-Dichlorobenzene
- Ethylene Dichloride
- Ethylene Glycol
- Trichlorethylene

Capacity:	1 kg/10 L of liquid
Cost:	$14.30/kg

AVAILABILITY & COMMERCIAL INFORMATION:

Developed by:	For:
Calspan Corporation Environmental Systems Dept. P.O. Box 400 Buffalo, New York 14225 Ph: (716) 632-7500 Tx: 91-270	Oil & Hazardous Materials Spills Branch, Industrial Environmental Research Lab. U.S. EPA Edison, New Jersey 08837 Ph: (201) 321-6634

PRODUCT: Chem-Gel **TYPE:** Gelling Agent

DESCRIPTION: A white, odourless polymeric powder that immobilizes chemicals in a gel that can be easily removed by mechanical means.

PHYSICAL SPECIFICATIONS:

Available Geometry:	Powder, flakes (drums or boxes)
Specific Gravity:	0.34
Storage Requirements:	Must be kept dry

OPERATING SPECIFICATIONS:

Toxicity:	Not known
Disposal:	Landfill or incinerate
Regeneration:	Cannot be regenerated

STATUS OF DEVELOPMENT & USAGE:
Marketed for many industrial sorbent applications.

PERFORMANCE:

Compatability:	Aqueous solutions, alcohols, polar and non-polar organics
Capacity:	Adsorption ratio of up to 100:1

Note: The gelling time is a function of the ratio of gelling agent to spilled chemical.

AVAILABILITY & COMMERCIAL INFORMATION:

Manufacturer:

Industrial Services Int'l Inc.
P.O. Box 10834
Bradenton, Florida 33507
U.S.A.
Ph: (813) 792-7778

Distributor:

Elmer Clark, Pres.
ES Clark Associates, Inc.
P.O. Box 40524
Jacksonville, Florida 32203
Ph: (904) 384-4393

PRODUCT: Indusorb

TYPE: Gelling Agent

DESCRIPTION: Light brown to white, odourless, polyacrylonitrile granules or flakes. It agglomerates chemicals into a gel easily removed by mechanical means.

PHYSICAL SPECIFICATIONS:
Available Geometry: Granules or flakes (drum or box)
Specific Gravity: 0.38

OPERATING SPECIFICATIONS:
Regeneration: Cannot be regenerated

STATUS OF DEVELOPMENT AND USAGE: Marketed for many industrial sorbent applications.

PERFORMANCE:
Compatability: Aqueous solutions of polar and non-polar solvents, acids, alkalis and hydrocarbon products
Capacity: 1 kg of agent gels 50 L of liquid

AVAILABILITY & COMMERCIAL INFORMATION:
Manufacturer:

Industrial Services Int'l Inc.
P.O. Box 10834
Bradenton, Florida 33507
U.S.A.
Ph: (813) 792-7778

Distributor:

ES Clark Associates, Inc.
P.O. Box 40524
Jacksonville, Florida 32203
Ph: (904) 384-4393

PRODUCT: Muck up Adsorbent **TYPE:** Solidifying Agent

DESCRIPTION: A tan coloured, water soluble calcium aluminum silicate (montmorillonite) granules that adsorb liquid to form a homogeneous, non-flowing mixture.

PHYSICAL SPECIFICATIONS:

Available Geometry:	Particles: 0.2% + 20 mesh, 1.5% - 60 mesh
Specific Gravity:	2.2
Shelf Life:	Indefinite
Storage Requirements:	

OPERATIONAL SPECIFICATIONS:

Toxicity:	Nontoxic (note pH 5.8)
Disposal:	Landfill
Regeneration:	Cannot be regenerated

STATUS OF DEVELOPMENT & USAGE: Marketed for cleanup of: water insoluble chemicals, PCBs, acids and caustics, bunker fuel, gasoline, paint, naptha, insecticides, rodenticides and fumigants.

PERFORMANCE:

Compatability:	Water insoluble products such as PCBs, toluene, and solvents
Cost:	$17.50/16 kg pail

AVAILABILITY & COMMERCIAL INFORMATION:
Manufacturer:

Mateson Chemical Corp.
1025 E Montgomery Avenue
Philadelphia, PA 19125
U.S.A.
Ph: (215) 423-3200

APPENDIX C

MOBILE PHYSIOCHEMICAL TREATMENT UNITS

APPENDIX C MOBILE PHYSIOCHEMICAL TREATMENT UNITS

(from Solsberg and Parent, 1986)

PRODUCT: EPA/MET-PRO Independent Physical/Chemical Waste-water Treatment System

DESCRIPTION: A mobile wastewater treatment system consisting of skid-mounted pumps, piping and vessels for long-term treatment of wastewater through neutralization, flocculation, sedimentation, carbon adsorption, filtration and disinfection. Coagulant and other chemicals can be added to the influent through a flash-mix tank. Solids separation follows in a flocculation tank and clarifier. Dissolved organics are removed in two activated carbon columns; the effluent is then polished in a pressure filter and disinfected in a chlorine tank.

PHYSICAL SPECIFICATIONS:

Skids:	Flocculation/ Clarifier	Adsorber/ Filter
Length (m)	4.6	7.5
Width (m)	3.0	3.0
Height (m)	3.1	2.7
Weight (kg)		
dry	5 454	7 727
operating	24 090	20 454

OPERATING SPECIFICATIONS:

Design Capacity: 189 m^3/day

Note: All operations, except the addition of chemicals and treating agents, are automatically controlled so that only one operator is required for chemical make-up, sludge disposal and general mechanical maintenance.

AVAILABILITY & COMMERCIAL INFORMATION:

Developed by:

Met-Pro Corporation
Systems Division
167 Cassell, Box 144
Harleysville, PA 19438
U.S.A.
Ph: (214) 723-6751

For:

Oil & Hazardous Materials
Spills Branch,
Municipal Environmental
Research Lab
U.S. EPA
Edison, NJ 08837, U.S.A.
Ph: (201) 321-6703
Contact: James J. Yezzi

PRODUCT: EPA Mobile Flocculation/Sedimentation System

DESCRIPTION: A trailer-mounted physical-chemical treatment system for flocculation, sedimentation, and filtration of suspended solid for pretreating wastewater contaminated with hazardous materials. Chemicals can be introduced into the system at various points into the long, looped pipe reactor. Static mixers in the reactor provide rapid mixing; effluent from the reactor is gently agitated in flocculation chambers, the floc collecting in a tube settler and discharged to a sludge collector; the wastewater finally passes through a tri-media filter which then must be treated to remove the hazardous materials.

PHYSICAL SPECIFICATIONS:

Dimensions:	Trailer is 12.2 m long Pipe reactor is 170 m long

OPERATING SPECIFICATIONS:

Capacity:	265 L/min.

AVAILABILITY & COMMERCIAL INFORMATION:

Oil & Hazardous Materials Spills Branch
Municipal Environmental Research Laboratory
U.S. EPA
Edison, NJ 08837
U.S.A.
Ph: (201) 321-6703

PRODUCT: Calgon Mobile Water Treatment Unit

DESCRIPTION: A trailer-mounted carbon adsorption system for the removal of dissolved organics from water. The wastewater is passed through beds of activated carbon. Effluent lines carry the treated water to the desired point of discharge.

PHYSICAL SPECIFICATIONS:

No. of vessels:	Single or Multiple vessels in series
Capacity:	Each vessel contains approx. 10 tons of granular activated carbon

AVAILABILITY & COMMERCIAL INFORMATION: Calgon Mobile Treatment Units are available on a lease basis through a 24-hour emergency phone number (412) 777-8000 for response to organic chemical spill.

Manufacturer:

Calgon Environmental
Systems Division
Calgon Corporation
Box 1346
Pittsburgh, PA 15230
U.S.A.
Ph: (412) 923-2345

Distributor:

Calgon Canada
27 Finley Road
Bramalea, Ontario
L6T 1B2
Ph: (416) 457-5310

PRODUCT: Activated Carbon Adsorber Water Purification System

DESCRIPTION: A packed bed of activated carbon for the removal of dissolved organics.

PHYSICAL SPECIFICATIONS:

	860-L system	3780-L system
Activated carbon		
Required (kg)	270	1360
Diameter (m)	1.22	1.68
Height (m)	2.18	2.41

OPERATING SPECIFICATIONS:

Operating Pressure (kPa)	103	103
Flow rate (L/min.)	38	189

AVAILABILITY & COMMERCIAL INFORMATION

Manufacturer:

Oil Recovery Systems, Inc.
299 Second Avenue
Needham (Heights), MA 02194
U.S.A.
Ph: (617) 449-5222

PRODUCT: PACT Mobile Waste Water Treatment System

DESCRIPTION: A mobile activated sludge/powdered carbon process for treating non-biodegradable and/or biodegradable organics. Powdered activated carbon is mixed with the activated sludge and wastewater in a contact-aeration basin. The carbon particles adsorb waste components that the micro-organisms cannot asimilate. The treated water is separated from the sludge and spent carbon through a clarifier and shallow-bed sand filter. Waste solids can be dewatered prior to disposal.

PHYSICAL SPECIFICATIONS:

Four mobile units are available:

Designation	Capacity (m^3/day)	Overall Dimensions (w x l x h (m))
PP- 50	189	2.4 x 12.3 x 4.9
PP-100	378	3.6 x 12.8 x 3.6
PP-200	757	3.6 x 12.8 x 3.6
PP-300	1136	3.6 x 12.8 x 3.6

OPERATING SPECIFICATIONS: The system takes two to three days to set up on site.

AVAILABILITY & COMMERCIAL INFORMATION:

Manufacturer:

Zimpro Inc.
Military Road
Rothschild, WI 54474
U.S.A.
Ph: (715) 359-7211
Tx: 29-0495
Contact: Industrial Sales Dept.

PRODUCT: EPA Mobile Physical/Chemical Treatment Trailer

DESCRIPTION: The system consists of two trailer-mounted systems for treating contaminated water. The unit consists of tanks for flocculation/sedimentation, filtration and carbon adsorption.

The contaminated water is pumped into a settling tank where flocculation and sedimentation occur. The clarified liquid is passed through mixed media filters, and carbon adsorption columns. Each step can be bypassed, depending on the needs of the specific wastewater.

PHYSICAL SPECIFICATIONS:

Unit No. 1:	13.7 m with three mixed media filters, three pressure carbon columns, pumps, piping, and a 100-kW generator.
Unit No. 2:	Smaller system, has one mixed media filter and one pressure carbon column.

Reaction/flocculation tank:	11 350 L
Sedimentation tank:	56 775 L
Dual Media Filters:	893 L
Carbon Columns:	19 600 L

OPERATING SPECIFICATIONS:

Unit No. 1:	6.3 to 37.8 L/s
Unit No. 2:	1.8 L/s
Area Requirement:	15 x 30 m

AVAILABILITY & COMMERCIAL INFORMATION:

Oil & Hazardous Materials Spills Branch
Municipal Environmental Research Laboratory
U.S. EPA
Edison, NJ 08837
U.S.A.
Ph: (201) 321-6703

PRODUCT: Demco Hydrocyclones

DESCRIPTION: A venturi effect is created within the cone which removes particulate matter from a fluid stream.

PHYSICAL SPECIFICATIONS:

Dimensions:

Cone:	Height:	0.522 m
	Max. Width:	0.225 m
	Weight:	22.7 kg
Silt Pot:	Height:	0.522 m

OPERATING SPECIFICATIONS:

Optimum pressure range corresponds to a flow rate of 26.5 to 34 L/s.

AVAILABILITY & COMMERCIAL INFORMATION:

Manufacturer:
Demco Incorporated
845 SE 29th Street
P.O. Box 94700
Oklahoma City, OK
U.S.A. 73143
Ph: (405) 631-1321

Distributor:
Demco Incorporated
9803-47 Avenue
Edmonton, Alberta
Canada
T6E 5M7
Ph: (403) 435-9251

PRODUCT: Mobile Ultra-Filtration Reverse Osmosis Unit

DESCRIPTION: A trailer-mounted, helicopter-portable Reverse Osmosis/Ultrafiltration unit for treating water contaminated with hazardous materials. Ultrafiltration (UF) is employed when filtering fine, suspended solids or oils. Reverse osmosis (RO) separates both suspended and dissolved solids plus biological oxygen demand (BOD) and chemical oxygen demand (COD) by permeating pure water through semi-permeable membranes. The permeate is returned to its original, uncontaminated source.

PHYSICAL SPECIFICATIONS:

The system consists of two banks of three pressure vessels, each containing up to two RO or UF membranes.

Weight:	1270 kg
Operating Environment:	-28 to 38°C

OPERATING SPECIFICATIONS:

Water Purification:	
RO	56.7 m^3/day from sea water
	113.5 m^3/day from brackish water
UF	284.0 m^3/day from contaminated water
pH range:	2 to 11

AVAILABILITY & COMMERCIAL INFORMATION:

Manufactured by:

Memtek Corporation
87 Bentley Ave.,
Nepean, Ontario
K2L 6T7
Ph: (613) 226-8381

For:

Environmental Emergencies
Technology Division
River Road Environmental
Technologies Centre
Ottawa, Ontario
Canada K1A 1C8
Ph: (613) 998-9622
Contact: Harry Whittaker

PRODUCT: Hollow Fiber Ultra-Filtration System

DESCRIPTION: A portable system capable of purifying contaminated water by filtration. The system consists of hollow fibre cartridges, permeate storage tank, circulation and backwash pumps. Designed for waste treatment in metal working, plating, chemical process and general industrial applications.

PHYSICAL SPECIFICATIONS:

Height:	1.702 m
Width:	1.118 m
Depth:	0.813 m
Electrical Requirements:	230 V, 30 to 60 Hz: 6.8A
	460 V, 30 to 60 Hz: 3.4A

OPERATING SPECIFICATIONS:

Operating pressure	172 kPa
Operating temperature	49°C
Recirculation rate	2.2 L/s

Other systems are available with production capacities of up to 142 m^3/day.

AVAILABILITY & COMMERCIAL INFORMATION:

Manufacturer:

Romicon, Inc.
Subsidiary of Rohm and Haas Company
100 Cummings Park
Woburn, MA 01801
U.S.A.
Ph: (617) 935-7840
Tx: 94-9333